

UNIVERSITY OF NOVA GORICA  
GRADUATE SCHOOL

**DEVELOPMENT OF VOC FREE UNIVERSAL  
COLORANTS FOR WATERBORNE AND  
SOLVENTBORNE DECORATIVE COATINGS**

MASTER'S THESIS

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## *Statement*

*I hereby declare that this is my original work and has not been submitted elsewhere.*

*Janez Virc*

## ACKNOWLEDGEMENT

I dedicate this work to my grandmother Ana Virc.





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## ABBREVIATIONS

VOC – volatile organic compound

REACH – Registration, Evaluation, Authorization and Restriction of Chemical substances

CLP – Classification, Labelling and Packaging Regulation

DSD – Dangerous Substances Directive

DPD – Dangerous Preparations Directive

HOS – hlapne organske snovi = VOC

DIN – Deutsche Industrial Norm

CIE – International Commission on illumination

L\* – lightness of the colour

a\* – defines the position of the colour on the red – green line

b\* – defines the position of the colour on the yellow – blue line

C\* – percentage of clean colour component

h\* – difference of colour

CMC – Colour Measurement Committee

dE\* – sum of colour difference in CIE colour space

ISO – International Standard Organisation

PVC – pigment volume concentration

CPVC – critical pigment volume concentration

B – base, is a product which is use to prepare the shade

B1 – whit base

B2 – low whit base

B3 – transparent base

B4 – yellow base

B5 – red base

FTIR – Fourier Transform Infrared

Haze – haze seen on enamels when it is dry on the surface

Gloss – gloss seen on coating when it is dry

$\rho_P$  – Density of a pigment

$\rho_B$  – Density of a binder

g – gram

DSC – Differential scanning calorimetry

F – Force

A – Area

$\tau$  – shear stress

$\eta$  – viscosity

$\dot{\gamma}$  – shear rate

## ABSTRACT

Colorants are key ingredients in making shades and enable a customer to choose among many different colours. This thesis discusses various ways in which we can prepare colorants. In the past and at the beginning of the mixing system (from 1950 to 1990), solventborne products were more common. In the last 20 years, the consumption of solventborne products has decreased while the consumption of waterborne products has increased. It used to be logical to have universal colorants in order to cover two systems: waterborne and solventborne. However, the consumption of a solventborne paint has been dropping every year due to environmental directives and also because people are becoming more aware of the fact that a waterborne paint is more acceptable in terms of health. Therefore we can expect that solventborne paints will most probably be removed from the decorative paint industry in the near future. It is difficult to predict the precise time when this will happen, but we can say that VOC-free universal colorants are already very much in demand in the decorative mixing systems. This paper shows one of the ways in which universal colorants can be prepared. We prepared four colorants from the following pigments:

- Inorganic red oxide (C.I.: P.R.101)
- Hybrid orange pigment
- Organic violet (C.I.: P.V.23)
- Organic magenta (C.I.: P.R.122)

It is important to get different batches as close as possible with regards to colour strength. For that reason we prepared also the filler paste which is required to optimize the strength of a colour. With our work we show that universal colorants can still play a big role in decorative coatings. Colorants were prepared for use on the market, which means that they can be placed into specific dispensing machines. A dispenser is a machine which doses different amounts of colorants in different combinations to mix a certain shade.

Since colorants are in dispensers for a longer period of time (1 to 3 months) we prepared colorants which did not sediment during this period. This means that our main methods and measurements were based on rheology parameters.

The colorants were tested in waterborne and solventborne paints. We carried out compatibility and wetting tests. We got very good result in compatibility and wetting tests with hybrid orange pigment, organic violet and organic magenta. Less good

result of compatibility and wetting tests were obtained with inorganic red oxide in solventborne products. Incompatibility can be fixed with the optimization of the base paint. The reason why we did not try to improve the compatibility of inorganic red oxide by changing the raw materials in the colorants was our focus of having as similar raw materials as possible in all four colorants.

We used rheology flow test for testing physical stability. For testing chemical stability we used FTIR spectroscopy and DSC (differential scanning calorimetry).

Having done all this work with colorants and tests in the systems (waterborne and solventborne), we were sure that universal colorants were still the right option in a decorative paint. With good results in the stove after 3 weeks at 40°C and with good results of compatibility and wetting tests in the base paints we showed that universal colorants can be used in order to have one colorant system on the dispenser machine.

We believe that different numbers of colorants and combinations of different technologies of colorants are vital for successful water and solvent based systems (with different types of products).

**Key words:** coatings, colorants, paint industry, pigments, dispensers, REACH, VOC.

## POVZETEK

### RAZVOJ UNIVERZALNIH NIANSIKNIH PAST BREZ HOS ZA VODNE IN TOPILNE SISTEME V DEKORATIVNIH PREMAZIH

Barvna industrija je zaradi evropske zakonodaje in osveščanja z vidika kemikalij pod neprestanim pritiskom po iskanju novih receptur za svoje produkte. Razvojno delo v razvojnih oddelkih barvne industrije je pospešeno, saj se razvojni inženirji trudimo pripraviti recepture, ki bi zagotovile kvaliteto in hkrati ustrezale novim okoljevarstvenim zakonom. Prva direktiva na področju dekorativnih premazov, ki je znatno narekovala korekcije in razvoj novih izdelkov, je bila *direktiva 2004/42/EC*. V direktivi je določeno, da se mora vsebnost organskih snovi, ki so hlapne pri temperaturi nižji od 250°C, znižati (za večino dekorativnih premazov).

Potrošnik se ob ponudbi različnih proizvajalcev lahko sreča z različnimi izdelki, ki pa imajo sicer isto funkcijo. Podobno je v barvni industriji. Proizvajalci barv ponujajo barvne izdelke na vodni in na topilni osnovi. Za oba sistema je tudi v dekorativnih premazih še dovolj zanimanja, da je izdelava produktov po obeh sistemih še ekonomsko upravičena. Pigmentne paste so do neke mere polizdelki, ki praviloma niso na voljo končnemu kupcu. Njihova glavna funkcija je, da nudijo možnost izdelave različnih barvnih odtenkov. Same po sebi niso uporabne, saj stabilni premaz tvorijo skupaj z drugim polizdelkom (bazo ali osnovo).

V kemiji poznamo pigmentne paste na vodni osnovi, na topilni osnovi in univerzalne pigmentne paste. Načinu izdelave nians na terenu (v trgovinah, skladiščih ali v proizvodnji), kjer gre za mešanje pigmentnih past in baze pravimo mešalni sistem. Mešalni sistemi so se z leti, razvojem in različnimi omejitvami spreminjali. Najprej so bili poznani mešalni sistemi, ki so omogočali niansiranje topilnih izdelkov. Kasneje so se pričeli uveljavljati tudi premazi na vodni osnovi (predvsem premazi za zidne površine), kar je sprožilo razvoj vodnih in univerzalnih pigmentnih past. V zadnjih letih se proizvajalci barv odločajo za različne variante mešalnega sistema. Razlike med njimi niso toliko v številu pigmentnih past, kot so v številu različnih tipov pigmentnih past. Tako se nekateri proizvajalci barv poslužujejo univerzalne pigmente paste, kombinacije vodnih in topilnih pigmentnih past, kombinacije vodnih in univerzalnih pigmentnih past ali tudi kombinacije vodnih, topilnih in univerzalnih. Če primerjamo število pigmentnih past, ugotovimo, da je v največ primerih

uporabljeno 16 različnih odtenkov. Uporaba 16 pigmentnih past na mešalnem sistemu predstavlja najboljšo pokritost barvnega prostora. Število pigmentnih past naraste v primeru, ko želijo proizvajalci zagotavljati širšo ponudbo tako vodnih kot topilnih izdelkov in ne uporabijo univerzalnih pigmentnih past. Praviloma pa število 32 različnih odtenkov ni preseženo, pri čemer je 16 pigmentnih past za topilni del in 16 za vodni del baz. Set 32 zagotavlja najširšo možno pokritost nians na topilnem kot tudi na vodnem delu.

Število pigmentnih past in s tem tudi število rezervoarjev je mogoče zmanjšati z uporabo univerzalnih past. Set 8 vodnih, 8 topilnih in 8 univerzalnih pigmentnih past zagotavlja isto število nians na različnih sistemih (vodni, topilni) kot set 32 past. Proizvajalci se seveda znotraj teh setov odločajo, kateremu delu (vodnem ali topilnem) bodo dali večjo težo, oziroma kateri del predstavlja večji tržni delež v njihovem primeru. Set 32 je redkost na trgu, saj pomeni drago vzdrževanje in začetno investicijo. Vsaka pigmentna pasta namreč mora imeti svoj ločen rezervoar, iz katerega se dozira. Trenutno je največ mešalnih sistemov s setom 16. Razlog, da se proizvajalci ne odločajo za širitev seta, je tudi v dragi opremi.

Predvsem pred omejitvijo količine hlapnih organskih spojin (HOS) in obstojnih anorganskih pigmentov na vremenske vplive je bila uporaba univerzalnih pigmentnih past logična izbira. Z uvedbo omejitev HOS in predvsem zahtev trga o obstojnih niansah na fasadnem sistemu so proizvajalci mešalnih sistemov pričeli z uporabo različnih kombinacij in kvalitet pigmentnih past. Izbira 16 univerzalnih pigmentnih past ni zadovoljila zahtevam po kvaliteti za fasadne sisteme, cenovni sprejemljivosti in hkrati široki pokritosti barvnega prostora. Formirali so se novi seti, v katerih skušajo proizvajalci zagotavljati optimalno kvaliteto in pokritost barvnega prostora, oziroma izbiro nians na obeh sistemih (izdelkih na vodni osnovi in izdelkih na topilni osnovi).

V tem magistrskem delu je predstavljena izdelava univerzalnih pigmentnih past.

Paste so pripravljene iz štirih pigmentov:

- Oksidno rdečega (C.I.: P.R.101) - anorganski pigment,
- Hibridnega oranžnega pigmenta,
- Organskega viola pigmenta (C.I.: P.V.23),
- Organskega magenta pigmenta (C.I.: P.R.122).



Priprava štirih univerzalnih pigmentnih past lahko predstavlja set 12 vodnih, 8 topilnih in 4 univerzalnih. Takšna kombinacija pigmentnih past ima to lastnost, da je mešalni sistem bolj naravnana na vodni del in malo manj na topilni del izdelkov. Po takšni razporeditvi je 16 pigmentnih past namenjenih izdelkom na vodni osnovi in 12 pigmentnih past izdelkom na topilni osnovi. Seveda je potrebno poudariti, da topilni del z 12 pigmentnimi pastami predstavlja tudi široko ponudbo različnih nians oziroma približno 75 % pokritost CIELab barvnega prostora.

Priprava 4 univerzalnih pigmentnih past v tem magistrskem delu ne izhaja iz razmišljanja, kako naj bi mešani sistem bil sestavljen, temveč je odločitev za pripravo prav izbranih štirih temeljila na osnovi različnih parametrov, kot so cena, poraba in različna kemija pigmenta. Torej, pomembna nam je bila predvsem pridobitev znanja o tem, kako se različni pigmenti obnašajo v podobnem okolju, s kolikor je mogoče podobnimi aditivi.

Z vidika cene smo se odločili za pripravo univerzalne viola in magenta pigmentne paste. P.V.23 in P.R.122 sodita med najdražje pigmente, posledično sta zato med najdražjimi tudi pigmentni pasti. Z možnostjo uporabe teh dveh pigmentnih past v obeh sistemih, tako vodnem kot topilnem, zagotovimo večjo rabo in s tem obračanje takšne pigmentne paste. Nianse, ki so narejene iz različnih pigmentnih past, imajo različno ceno. Zato se porabniki pogosto na mešalnem mestu za določeno nianso odločajo tudi na osnovi cene. Iz tega razloga se pri izdelavi receptur za nianse proizvajalci barv izogibajo večjim količinam uporabe viola in magenta pigmentne paste v recepturah. Ob možnosti uporabe viola in magenta pigmentne paste v vodnem kot tudi topilnem sistemu se zagotovi večja možnost porabe. Že manjši dodatki tako viola kot magenta pigmentne paste spremenijo odtenek nianse (kar tudi pomeni manjšo porabo). Vsekakor za proizvajalce, ki nudijo topilni kot tudi vodni sistem, ni smiselno, da bi ponujali dve viola pigmentni pasti, eno za izdelke na vodni osnovi in drugo za izdelke na topilni osnovi, isto velja za magento.

Pri izbiri pigmentov smo želeli videti tudi razliko med pripravo pigmentnih past iz anorganskih pigmentov in iz organskih pigmentov. Oranžen pigment, za katerega proizvajalec trdi, da je hibriden, ni definiran niti kot organski niti kot anorganski pigment. Po zagotovilih proizvajalca naj bi kazal bolj anorganske lastnosti pigmenta, kar naj bi pomenilo tudi, da zagotavlja boljše vremensko obstojnost. Proizvajalci pigmentov so se odločili za dodatno obdelavo ravno oranžnega pigmenta, ker je

uporaba le-tega z vidika možnosti vsečnih nians narasla. Končni uporabniki se pri nakupu nians za notranje kot tudi zunanje površine največkrat odločajo za nianse, v katerih nastopa prav oranžni pigment. Tipični anorganski pigment je P.R.101 oksidno rdeči. Značilna razlika pri pripravi pigmentnih past iz anorganskih ali organskih pigmentov je v različni koncentraciji pigmenta v recepturah. Za pigmentne paste z anorganskimi pigmenti tako velja, da je koncentracija pigmenta večja. Sicer zavisi od pigmenta oziroma pigmentne paste, vendar je v povprečju koncentracija dvakrat večja. Z izdelavo pigmentnih past, ki se razlikujejo v kemiji pigmenta, smo želeli pridobiti informacijo, ali je težavnost izdelave pigmentne paste lahko povezana tudi z uporabo različnih pigmentov v njihovi kemiji (organski, anorganski). Z delom, ki smo ga opravili, ne moremo presoditi, da je izdelava pigmentne paste lahko enostavnejša z anorganskimi kot z organskimi ali obratno.

Na začetku smo se lotili viola pigmenta (C.I.: P.V.23), kjer smo ugotovili, da potrebujemo polnilo. Še boljša rešitev kot izdelava polnila je bila izdelava polnilne paste, ki je v bistvu polnilo v stabilni tekoči obliki z viskozni in reološkimi lastnostmi podobnimi pigmentnim pastam. Izdelava polnilne paste se je pokazala kot dobra rešitev, saj smo jo lahko uporabili kot surovino za urejanje kolorističnih lastnosti pigmentnim pastam. Urejanje kolorističnih lastnosti je predvsem nujno v proizvodnji, kjer so lahko odstopanja od šarže do šarže večja, in je zato rešitev s pomočjo polnilne paste toliko bolj potrebna.

Laboratorijsko delo smo usmerili v pripravo stabilne polnilne paste, ko smo skozi razvoj univerzalnih past ugotovili, da je to najbolj primerno. Stabilnost polnilne paste kot tudi pigmentnih past smo preverjali s pomočjo reoloških parametrov, ki so nam že bili v pomoč pri izdelavi drugih produktov. Čeprav je poznanih več reoloških testov smo se odločili za merjenje tokovnih krivulj, ki so nam dale informacije o stabilnosti posameznih vzorcev. Meritev tokovnih krivulj smo opravili pred staranjem vzorca in po staranju vzorca v peči pri 40°C od 1 do 4 tednov. Vzorce, pri katerih se viskoznost po staranju ni spremenila za 0,3 Pas ali več pri strižni napetosti od 10 do 10<sup>3</sup>, smo smatrali za stabilne.

Ko smo uspeli narediti stabilno pigmento pasto, smo vsako pasto testirali v vodnem in topilnem sistemu. Naredili smo test kompatibilnosti, pri čemer smo vzorec mešanice baze in pigmentne paste v stresalniku stresali 5 minut. Takšen vzorec smo nato z nanašalcem nanесли na površino. Pri vseh vzorcih smo izbrali debelino nanosa

200 µm. Vzorce smo nanašali na bel karton. Preden je vzorec kazal prve znake sušenja smo s prstom, s pritiskom na nanosen vzorec s krožnimi gibi, zarisali kroge - tako imenovan RUB-OUT. Test pokaže, kako homogen je vzorec. Kolikor večja je razlika v niansi in jakosti nianse med površinama v krogu in izven njega, toliko manj je naš vzorec homogen. To pomeni, da pigmentna pasta ni dobro vmešana v bazo, oziroma ni prave kompatibilnosti med bazo in pigmentno pasto. Drugi test omočljivosti nam poda podobno informacijo o možnosti mešanja določene pigmentne paste in baze. Test poteka tako, da se pripravi vzorec, ki se stresa-meša 3 minute in isti vzorec, ki se ga stresa-meša 10 minut. Vzorec po različnem času stresanja smo nanesli na površino (debelino nanosa 200 µm) črno belega kartona in merili razliko v niansi in barvni jakosti med vzorcem, ki smo ga tresli 3 minute in tistim, ki smo ga tresli 10 minut. Manjša kot je razlika med vzorcema, boljši je rezultat in pomeni, da sta baza in pigmenta pasta med seboj kompatibilni.

Izdelki, ki smo jih izbrali za testiranje kompatibilnosti in omočljivosti s pigmentnimi pastami so:

- fasadna barva (izdelek na vodni osnovi),
- notranja zidna pralna barva (izdelek na vodni osnovi),
- lak lazura (barva za les, izdelek na topilni osnovi),
- emajl za kovino in les (izdelek na topilni osnovi).

Kompatibilnost kot tudi omočljivost je bila sprejemljiva z oranžno, violo in magenta pigmentno pasto. Z oksidno rdečo pigmentno pasto je bila kompatibilnost kot tudi omočljivost slabša s topilnima izdelkoma. Pri testu, med katerim smo vmešali vse štiri pigmente paste, je bila kompatibilnost kot tudi omočljivost ustrezna. Izhajajoč iz tega, smo odločili, da je oksidno rdeča pigmenta pasta za uporabo v sistemu ustrezna. Tudi zato se za spreminjanje recepture oksidno rdeči pigmentni pasti nismo odločili. V primerih, ko imamo fizikalno stabilno pigmentno pasto, je bolj ustrezna sprememba in optimizacija na bazah.

S testi omočljivosti in kompatibilnosti smo lahko zaključili, da smo pripravili univerzalne pigmente paste. Rezultate smo potrdili z meritvami s spektrofotometrom. Meritve so bile znotraj kolorističnih odstopanj. Pri kolorističnih mejah smo upoštevali dE in barvno jakost. Sprejemljiv odstop za dE smo določili od 0 do 1. Sprejemljiv odstop za barvno jakost smo določili od 95 do 105%. Potem, ko smo

vedeli, da smo pripravili univerzalne pigmente paste, ki kažejo fizikalno stabilnost, smo se odločili, da pigmentne paste testiramo tudi v disperzerju.

Disperzer je naprava, ki se uporablja za doziranje pigmentih past v določenih količinah, kot predpisuje receptura za določeno nianso. Vse štiri pigmente paste smo tako testirali tudi v takšni napravi, pri čemer smo spremljali točnost doziranja po enem tednu, po treh tednih in po treh mesecih. Prav tako smo spremljali morebitno zgoščevanje v rezervoarju oziroma dvig viskoznosti, ki lahko onemogoči mešanje ali celo prepreči doziranje. Rezultati so bili za vse štiri pigmente paste ustrezni, pri čemer je obstajala manjša razlika med njimi. Tako sta oranžna in magenta pigmentni pasti kazali znake dviga viskoznost po treh mesecih. Vendar pa ta dvig viskoznosti ni pomenil težav pri mešanju in doziranju teh pigmentih past. V interesu proizvajalca kot tudi prodajalca je, da se pigmentne paste trošijo, ker to omogoča, da je v rezervoarju vedno sveža pigmenta pasta; to je tudi ključno za ohranitev kvalitete v rezervoarju kot tudi naprej v niansi.

Ob testiranju naših vzorcev z reološkimi testi smo predvsem iskali informacijo, kako fizikalno stabilni so naši vzorci. Vendar smo, ker z reološkimi testi lahko o kemijski stabilnosti vzorcev zgolj ugibamo, z vzorci naredili tudi FTIR spektroskopijo in DSC kolorimetrijo. Obe metodi sta potrdili, da so naši vzorci kemijsko, kot samostojni produkti, stabilni. Prav tako pa smo z metodami dokazali, da so naši vzorci kemijsko kompatibilni z izdelki na vodni osnovi kot tudi z izdelki na topilni osnovi.

Naš cilj je bil pripraviti fizikalno in kemijsko stabilne univerzalne HOS (hlapne organske spojine) proste pigmente paste. Lahko zaključimo, da smo bili dokaj uspešni, kljub in tudi zaradi minimalne vsebnosti HOS (manj od 1 %). Pri izbiro surovin ni bilo vedno mogoče predvideti, če bo uporaba določene surovine prispevala k HOS-u, zato se ni bilo mogoče določenim surovinam izogniti (proizvajalci surovin ne navajajo vedno vsebnosti HOS). Drži tudi, da je zagotovitev stabilnosti s surovinami, ki vsebujejo HOS, lahko tudi hitreje dosegljiva. Naše naslednji cilj bo tako izločiti oziroma zamenjati surovine, ki doprinesejo k HOS. Cilje je bil dosežen z vidika, da je dovoljena minimalna vsebnost HOS 30 g/liter. Naši izdelki so dosegli HOS vrednosti med 4,4 in 9,5 g/liter. Iz tega sledi, da se bo vsakemu izdelku, kateremu bomo dodali naše kolorante in ima vsebnost HOS nad 9,5 g/liter, z dodatkom naših kolorantov ta vsebnost na liter znižala.

Seti pigmentnih past se od proizvajalca do proizvajalca razlikujejo. Nekateri proizvajalci so bolj prepoznavni z izdelki na vodni osnovi drugi z izdelki na topilni osnovi. Drugi, še večji faktor pri doseganju premoči v okviru mešalnega sistema, pa so različna tržišča, ki imajo različne potrebe in zakonodajo.

S tem magistrskim delom smo želeli pokazati, da je izdelava univerzalnih pigmentnih past brez hlapnih organskih spojin pod 250°C smiselna in da prinaša mnoge možnosti, ki so ekonomsko in okoljevarstveno upravičene.

Mešalni sistem iz več razlogov predstavlja kompleksen sistem, ki proizvajalcem odpira nešteto vprašanj. Skozi delo in spoznavanje različnih sistemov smo se naučili, da bo najbolj uspešen tisti proizvajalec, ki bo lahko hitro reagiral na različne potrebe trga. Hiter odziv omogočajo različni seti in kombinacije le-teh, kar seveda pomeni tudi nujno uporabo univerzalnih pigmentnih past.

**Ključne besede:** premazi, pigmente paste, mešalni sistemi, barvna industrija, pigment, REACH.



## 1. Introduction

Decorative coatings (architectural coatings) are widely used for decoration and protection of buildings, architectural components and building parts made of various materials. Walls (interior or exterior) are painted in order to hide visible defects, provide a nice and homogeneous appearance and ensure the required level of protection to the substrate against various aggressions (dirt, humidity, etc.). Besides their basic functions, coatings are also used for decorative purposes and should offer various optical properties (e.g. haze, gloss, etc.) and the best colour development. Painting and decoration have been made easier with the development of many easy-to-use products. In order to reduce the risk for the environment and the user Directive 2004/42/EC limits the VOC content of these widely used products [1]. In the paint industry research departments have been putting a lot of effort into the development of new products that would comply with VOC regulations. The challenge is very demanding as new approaches need to be developed and novel additives should be used.

Colorants are used for tinting the base paint to the customer's desired shade. Colorants are pigment dispersions with defined colouristic and rheological properties essential for a successful use in dispensing machines. They can be universal, waterborne or solventborne.

For the scope of this master thesis we developed low VOC universal colorants. An important advantage of universal colorants is a high degree of compatibility in a variety of water and solvent based paints. VOC free universal colorants play an important role in the required reduction of VOC content in paint. Low values of volatile organic compounds (VOC) are important from the users' point of view. Lower VOC means that painter is less exposed to harmful volatile organic compounds.

This thesis is mainly focused on four universal colorants with the following pigments in use: inorganic red oxide (C.I.: P.R.101), hybrid orange pigment, organic violet (C.I.: P.V.23) and organic magenta (C.I.: P.R.122).

The thesis describes the preparation of colorants which are compatible with waterborne and solventborne paints (bases).

### **Use of colorants, tinting systems**

Colorants are the second most important component that makes the colour mixing possible in every store. Since we all have a different opinion about what the best colour shade and colour combination for our wall would be a colour tinting system was established. To avoid expensive colour shades production, the tinting system has to be moved out of the production plant and also be made affordable for its users.

The above needs raised questions in the industry and resulted in research aimed at finding out the way to satisfy the customers also within an acceptable economic frame. For this reason the tinting system in the colour industry was invented. The tinting system was launched in bigger quantities in the 1950's in USA and in the 1960's in Europe. The system as it is known now is composed of base paints, colorants, colour formulae, tinting equipment and software.

Base paints are paints whose colour and colour strength are controlled. Colorants are added to the base paint to create a certain colour shade. Depending on the desired colour range, usually one to four white and transparent bases paints are required for each product. In some cases the bases are also red and yellow in order to achieve good opacity of the coating.

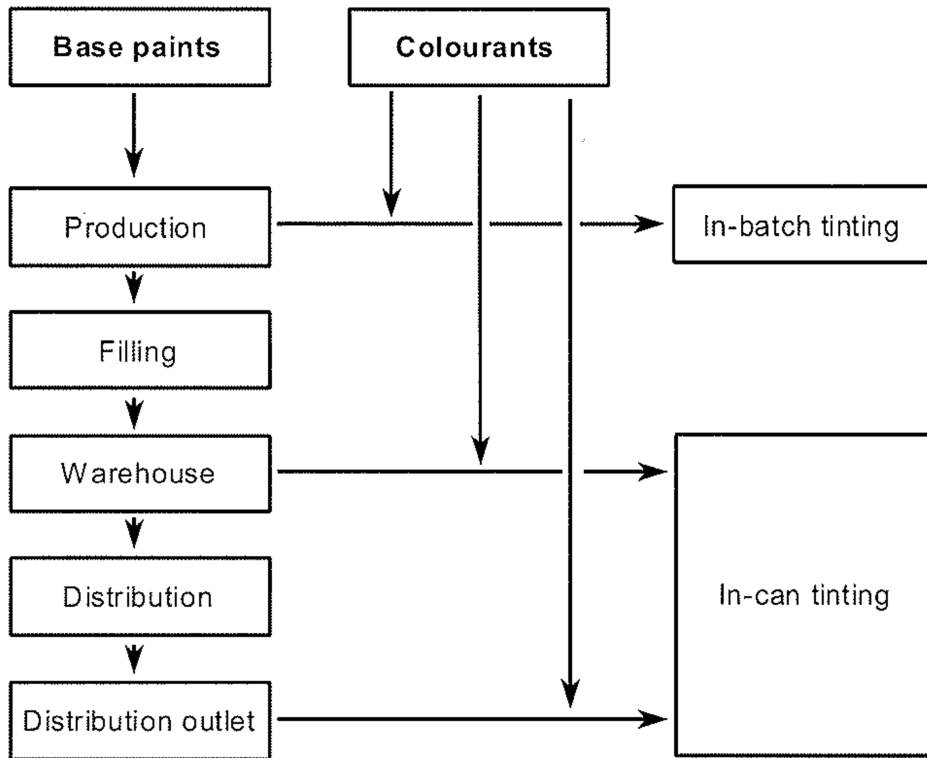
Colorants are pigment concentrates kept in a strictly controlled liquid state. The colour strength and rheology are constant. Colorants are developed to be compatible with a wide range of different types of paint products.

Colour formula defines the combination of colorants to be added to a certain amount of a base paint in order to create a certain colour shade. With colour formula the same colour shade can be produced correctly time after time.

Equipment in tinting system is dispenser and mixer. A dispenser can have a different number of canisters (usually from 8 to 32, at the moment 16 is most widely used in the market) with volume from 1.5 litres to 5.0 litres. After adding colorants to the base, we also have to mix the can and that is done using a mixer, gyroscopic mixer or stirrer. The mixer is mostly in use in small shops where 1 to 5 litres cans are mixed because they are most frequently sold. The gyroscopic mixer is better for bigger cans of 10 to 20 litres and for plasters. The stirrer is used in the production plant and is also coming to the market in bigger stores where they mix bigger quantities of plasters in twenty-litre cans.



Software is used to manage the colour formulae and the production of colours. It has the function of telling the dispenser what to do. A spectrophotometer with software can be used to create new colour formulae at the point of sales.



**Figure 1:** Alternatives when using a tinting system.

Figure 1 shows tinting systems alternatives. In this thesis we focus on in-can tinting. However, as can be seen from Figure 1 tinting system is very much present also in a production plant where they have ready-made shades. Moreover tinting is present in warehouses where a bigger amount of one shade needs to be prepared.

There are many producers in the market offering in-can tinting. Table 1 shows some producers that offer different systems. The information is collected from a public sources and an internal evaluation of some competitors.

**Table 1:** Mixing system from different producers.

Producer of mixing system	Producer 1	Producer 2	Producer 3	Producer 4	Producer 5	Producer 6	Producer 7
Number of canisters	16	16	16	32; 19; 16	24	32; 18	16;
Colorants waterborne solventborne universal	Universal	Waterborne	Universal	Waterborne universal	All three	Waterborne universal	Universal
Organic colorants; Inorganic colorants.	5; 11	6; 10	10; 6	13; 19	N.A.	N.A.	N.A.
One producer of colorant and bases paints	YES	NO	YES	NO	NO	N.A.	N.A.
Number of exterior shades	600	2000	300	2000	N.A.	1350	4500
Number of product on the system	17	30	27	25	N.A.	N.A.	25
Products waterborne; Products solventborne	14; 3	30	1-20; 2-7	18;7	N.A.	N.A.	N.A.
Accuracy of shades	90.00%	99.90%	95.00%	99.00%	N.A.	N.A.	N.A.
Spectrophotometer	HH 400X	Not offering	Not offering	Not offering	Not offering	Match STICK	Not offering
Packing of colorant	1 litre	1 litre	1 litre	1 litre	1 litre	N.A.	N.A.

N.A. – Information not available.

It is more or less necessary to have a 16-canister model in order to cover as much of the colour space as possible. The 16-canister model is also the most optimal from the point of use where all 16 colorants are normally used in the same volume. With 16-canister mixing systems shades recipes can be prepared in the way to insure the use of all colorants. In majority of paint producers decided to have a 16-canister mixing system which was universal. This trend was present 15 to 20 years ago. Producers who later decided to have a mixing system normally chose waterborne colorants. The trend to have a waterborne system is more or less logical due to environmental legislations. However universal system is still very much present since many producers could not find a quality replacement for solventborne long oil alkyds enamels. There are some alternatives to satisfy market needs. One way is to make

high solid enamels with the limit of VOC (400 g/l and 300 g/l) as shown in Table 3. Therefore the future of universal colorants seems to be longer than one could have predicted since in small volumes universal colorants can also be used in high solid enamels.

Organic and inorganic pigments in colorants were chosen due to their weather stability. Now the trend is to have more inorganic pigments which help achieve a better weather stability of exterior facade paints. In the past there were less inorganic pigments because colorants were mostly used for solventborne enamels which had on average almost 60 % of resin. This high per cent of resin in enamels ensures good weather stability also to organic pigments. It is different for exterior facade paints in which the percentage of resin is normally 30 %. This means a worse protection of the pigment with the resin. Therefore the paint producers in order to achieve a better weather stability with their facade paints started using inorganic pigments in their colour shade recipes. Another reason for that is also that customers are now willing to have colourful outdoor surfaces (facade wall, roof, fence, windows), which was not so common in the past.

At the start of the mixing system there were companies which produced colorants, companies which produced base paints for the colorants and companies with equipment. Their partnership was offering a mixing system. Over years of experience and information about the system many producers decided to offer their own mixing system. This means producing by themselves the colour base and as well as the colorants. This approach has given certain advantages to those who have decided to do so. The first advantage is that they can offer lower prices than the competitors. They can also react much faster when a problem appears. Currently it seems that any producer who wants to be successful with the mixing system should have a comprehensive offer which includes all the required products (base, colorants, colour formulation and dispensers).

To have a successful mixing system it is also important to offer accurate colour shades. Colour cards play an important role here. If they are made of materials on which colours are later really applied they can ensure more accuracy than otherwise: when colour shades on a colour card are presented with another material. The difference is in surface and gloss and these two factors can very much affect the look of a colour shade on a colour card and the one we get from the required material.

Another factor ensuring the accuracy is the preparation of the recipes for the colour shades. To get the precise colour shade as is shown in the colour card it is normally necessary to make the recipe by testing the colorants in the paint. Since this costs a lot of money and takes a lot of time, recipes are normally handmade and calculated mathematically with a program which knows which colorant and in what amount should be added in order to get the correct colour shade.

Some producers have already made a step forward and started with the mixing system spectrophotometer which can choose for the end consumer the recipe for the colour shade a consumer wants. Normally a consumer brings some piece of metal or wood which is coloured with a certain colour shade that cannot be found on colour-cards. That piece is measured with the spectrophotometer and with the data in its program a recipe for a certain colour shade is calculated. The precision of the result depends on the quality of the saved data which are in the program for a certain product.

Another important part of the mixing system is the quality of the dispensing machine. The dispenser has to ensure good repeatability. In decorative coating dispensers have normally canisters with the volume of 1.5 to 3.5 litres. To avoid most of the problems with colorants on the dispensing machine it is important that consumption of the colorants is ensured. Consumption of the colorants is achieved by offering many different products and forming the recipes in such a way that the average consumption of every colorant is not too different from another. In this way we avoid the sedimentation and the raising of viscosity of the colorant in the canisters, which is a usual defect if the colorant stays in the canister too long.

## **1.1. Restrictions in decorative paint industry**

In the decorative paint industry we have many restrictions which are described in REACH, CLP and VOC directives.

### **1.1.1. Registration, Evaluation, Authorization and Restriction of Chemical substances**

REACH is the European Community Regulation on chemicals and their safe use. It deals with the **R**egistration, **E**valuation, **A**uthorization and **R**estriction of **C**hemical substances. The law was enforced on 1 June 2007 [2].

The aim of REACH is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. At the same time, REACH aims to enhance innovation and competitiveness of the EU chemicals industry. The benefits of the REACH system will come gradually, as more and more substances are phased into REACH.

The REACH Regulation places greater responsibility on industry to manage the risks from chemicals and to provide safety information on the substances. Manufacturers and importers are required to gather information on the properties of their chemical substances, which will allow their safe handling and registering the information in a central database run by the European Chemicals Agency (ECHA) in Helsinki. The Agency acts as the central point in the REACH system: it manages the databases necessary to operate the system, co-ordinates the in-depth evaluation of suspicious chemicals and is building up a public database in which consumers and professionals can find hazard information.

The Regulation also calls for the progressive substitution of the most dangerous chemicals when suitable alternatives have been identified.

One of the main reasons for developing and adopting the REACH Regulation was that a large number of substances have been manufactured and placed in the market in Europe for many years, sometimes in very high amounts, and yet there has been insufficient information on the hazards that they pose to human health and the environment. There is a need to fill these information gaps to ensure that industry is

able to assess hazards and risks of the substances, identify and implement the risk management measures to protect people and the environment.

It has been known and accepted since the drafting of REACH that the need to fill the data gaps would result in an increased use of laboratory animals for the next 10 years. At the same time, in order to minimise the number of animal tests, the REACH Regulation provides a number of possibilities to adapt the testing requirements and to use existing data and alternative assessment approaches instead.

REACH provisions are being phased-in over 11 years. Companies can find explanations of REACH on the ECHA website, in particular in the guidance documents, and can contact national helpdesks [2].

### **1.1.2. Classification, labelling and packaging**

CLP Regulation stands for Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures, amending and repealing directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (REACH). It came into force on 20 January 2009 and applies across the European Union [3].

The provisions of CLP will replace Council Directive 67/548/EEC (Dangerous Substances Directive, DSD) and Directive 1999/45/EC (Dangerous Preparations Directive, DPD) in a stepwise approach.

The differences between CLP and DSD/DPD are due to the integration of the terminology, classification criteria and labeling elements of the United Nations' Globally Harmonised System (UN GHS) and to procedures taken over from the REACH Regulation. An overview of the most important differences is included in Table 2 [3].

**Table 2:** Important differences between the DSD / DPD legislation and the CLP Regulation [3].

<b>DSD - Dangerous Substances Directive/ DPD - Dangerous Preparations Directive</b>	<b>CLP - Classification, labelling and packaging</b>
<b>Terminology</b>	
DSD terminology, e.g. preparation, dangerous, category of danger, risk phrase, safety phrase	UN GHS terminology, i.e. mixture, hazardous, hazard class, hazard statement, precautionary statement
<b>Criteria</b>	
DSD categories of danger for physical, health and environmental hazards	UN GHS hazard classes including those differentiations which best reflect the DSD categories of danger; total number of hazard classes higher under CLP than the total number of categories of danger under DSD
DSD categories of danger plus additional labelling elements, e.g. R1 (“Explosive when dry”)	UN GHS hazard classes plus supplemental labelling elements taken over from DSD e.g. EUH001 (“Explosive when dry”)
DPD calculation rules (“conventional method”) for the classification of preparations	UN GHS calculation methods (additivity, summation) deviating from the DPD calculation rules
Testing, human experience or calculation for mixture classification	Similar to DPD; in addition bridging principles that allow the classification of mixtures on the basis of data on similar tested mixtures and information on individual hazardous ingredient substances
<b>Labelling elements</b>	
DSD symbols	CLP pictograms
Selection out of 50 different safety phrases; limited flexibility of selection	Selection out of 110 different precautionary statements; flexibility of selection
<b>Procedures</b>	
If harmonised classification then normally for all categories of danger	If harmonised classification then for substances which are carcinogenic, mutagenic, toxic to reproduction or respiratory sensitisers; other effects on a case-by-case basis
Harmonised classification based on a Member State proposal	Harmonised classification based on a Member State proposal (provisions previously contained in REACH) or a proposal by a manufacturer, importer or downstream user under certain conditions
No notification procedure foreseen	Notification of the classification and labelling of substances to the Classification & Labelling Inventory established by ECHA (provisions previously contained in REACH)

### 1.1.3. Volatile organic compounds

Volatile organic compounds – VOC directive is one of the regulations which directly make positive effects on the environment as well as on the users. Until 2007 there was no VOC limit in Europe for decorative coatings. The first regulation on VOC was made in 1999 (Directive 1999/13/EC) for the reduction of industrial emissions of volatile organic compounds (VOCs) in the European Union. At that time it covered a wide range of solvent using activities, e.g. printing, surface cleaning, vehicle coating, dry cleaning and manufacture of footwear and pharmaceutical products. The original VOC Solvents Emission Directive (Directive 1999/13/EC) has been amended. Article 13 in Directive 2004/42/EC has removed subjectivity of Vehicle Refinishing and for that reason products fall under the scope of the Paints Directive (Directive 2004/42/EC) [1].

VOC is any organic compound with an initial boiling point lower than or equal to 250°C measured at the standard atmospheric pressure of 101.3 kPa. Directive 2004/42/EC establishes limit values for the maximum VOC contents in decorative coatings. The first set of limit values is dated 1 January 2007 and the second 1 January 2010.

As can be seen from Table 3 in some cases there is a big difference between the limit in 2007 and the limit in 2010. Product sectors coloured in blue are those we have affected with our new development of VOC-free colorants. With VOC-free colorants we are lowering down also the VOC values in basic products since the final coatings are in these cases made of a base paint and a colorant.

Using the data in Table 3 we employ the following formula for calculating VOC in a coating:

$$VOC = \sum_{i=1}^{i=n} m_{i(\text{solvent in the sample})} \cdot \rho_{\text{sample}} \cdot 1000$$

**Equation 1:** Formula for calculating VOC value in a sample [1].

$m_i$  – Weight of solvent which is used in the recipe of the sample (coating), is the mass, in grams, of compound  $i$  in 1 g of the test sample [1].



**Table 3:** 2007 and 2010 limits of VOC in decorative coatings by the Directive 2004/42/EC.

Name of the group	Category	Type	MAX VOC in 2007 (g/l)	MAX VOC in 2010 (g/l)
Inside mat wall and roof. (Gloss <= 25% measured on angle 60°)	a	WB	75	30
	a	SB	400	30
Inside mat wall and roof. (Gloss >25% measured on angle 60°)	b	WB	150	100
	b	SB	400	100
Outside wall	c	WB	75	40
	c	SB	450	430
Inside/outside coatings for wood or metal decorative	d	WB	150	130
	d	SB	400	300
Inside/outside lacquers and bark-liquor for wood, including mat bark-liquor for wood	e	WB	150	130
	e	SB	500	400
Inside and outside thin bark-liquor for wood	f	WB	150	130
	f	SB	700	700
Basic coatings	g	WB	50	30
	g	SB	450	350
Resin basic coatings	h	WB	50	30
	h	SB	750	750
Special one component coatings	i	WB	140	140
	i	SB	600	500
Two component coatings with reactive feature for special end use (floor)	j	WB	140	140
	j	SB	550	500
Coatings with decorative features	l	WB	300	200
	l	SB	500	200

\*SB – Solventborne, WB - Waterborne

## 2. Purpose of this thesis

It is necessary to use universal colorants in order to easily meet all the needs that customers have with the colour mixing system. The purpose of this thesis was to prepare low VOC (volatile organic compound) universal colorants that could be used with solventborne and waterborne paints. Preparing VOC-free colorants is indispensable, especially in decorative coatings where main users are people whose first profession is not painting. The second reason why we were aiming to prepare VOC-free colorants lays in the trend of environmental legislation, which forces paint industry to reduce the VOC levels in all of their products.

An important aspect was to prepare a set using only four universal colorants together with others solventborne or waterborne colorants. This way one has the option to have two sets with 14 colorants for each system with 24 canisters dispensers when using for settling a combination with 10 solventborne and 10 waterborne colorants.

Our task was to prepare completely stable and practically useful universal colorants. This means the colorant had to be prepared in a production plant and tested also in dispensers; in order to prove a possible commercial use.

Another goal which we were after was the preparation with as good economic value recipe as possible.

To sum up the objective of this thesis: the goal was to achieve four stable colorants (this means that the colorants will not sediment in the canister) whose viscosity will not rise too much (more than 0.3 Pas at shear stress between 10 to  $10^3$  Pa, depends from the sample) in short time of testing in the stove and in the dispenser. Moreover the result of the compatibility and wetting tests in the waterborne and solventborne systems should show no compatibility and wetting problems. Our aim was to prepare colorants with as high concentration of a pigment as possible and with acceptable rheological properties in order to achieve a higher efficiency of the colorants.

The results from this study should help evaluate possible scenarios on the market: the use of solventborne, waterborne and universal colorants based mixing systems.

### **3. Experimental sample preparation**

There are many methods which can be used in the paint industry to obtain information about the quality of a product. The quality of the universal colorants can also be measured using the same methods if not directly then when preparing the paint with colorants in it. Methods depend on the purpose of usage. Universal colorants, like other different types of colorants, can be called semi-manufactured goods, because they are used only when they are mixed in another semi-manufacture called base. That is why there are many methods which are the same as for coatings. Colorants are mixed in the paint to give a certain shade, but they can also affect characteristics of a coating.

#### **3.1. Testing of universal colorants in base paint**

We used the following base paints: interior waterborne wall paint styrene acrylic dispersion, exterior waterborne wall paint styrene acrylic dispersion, solventborne paint for metal long-oil alkyd and solventborne paint for wood long-oil alkyd. We checked compatibility with those products in the bases. Solventborne products in which we tested have three bases: the first B1 has 20 % of TiO<sub>2</sub>-pigment and the second B2 9 %. From the point of view of pigmentation only the third base B3 is the same in all the four products. For solventborne paints we decided to choose B3 for our main testing matter.

The base paint adaption starts by testing the wetting and colour acceptance of the colorants with the paints chosen for the tinting system. When adding colorants to base paints, resins, solvents and additives are mixed and the results can never be completely anticipated.

**Table 4:** Base paints in which colorants were tested.

Brand	Resin classification	VOC limit before 2007	VOC limit after 2007	VOC limit after 2010
Interior (waterborne, wall paint)	Styrene Acrylic dispersion	More than 75 g/l	Less than 75 g/l	Less than 30 g/l
Exterior (waterborne, wall paint)	Styrene Acrylic dispersion	More than 75 g/l	Less than 75 g/l	Less than 40 g/l
solventborne, paint for metal	Long-oil alkyd	More than 400 g/l	Less than 400 g/l	Less than 300 g/l
solventborne, paint for wood	Long-oil alkyd	More than 500 g/l	Less than 500 g/l	Less than 400 g/l

The interior waterborne wall paint was one of the testing matters. The recipe structure for this product consists of: resin, pigment, dispersing agent, fillers, water and defoamers. Resin is water based styrene-acrylic with solid content 50 % (ISO 976) and viscosity 1,800 mPa.s (ISO 2555 Brookfield Viscometer). There are three bases for this product with which we can make all the colour shades we want. We could use only one without the pigment (without B1 and B2), but this would not be cost acceptable, since colorants are more expensive than ready-made colours. The two other bases are produced to get less expensive colour shades and also create the final product with a better opacity. It is also true that it is better to add colorants in low quantities in order to retain the quality of the paint at the same level as established at the creation of the base paint. For waterborne paints we use base B1 with the white pigment. Out of all the three bases B1 has the biggest per cent of the white pigment and is therefore used in preparation of colour shades with a lower amount of colorants.

The recipe for the exterior waterborne wall paint consists of: resin, pigment, dispersing agent, fillers, water and defoamers. Resin as the most important component since it gives the main properties and characterization to the coatings is in this product styrene-acrylic with different optimization. Moreover, we have three

base paints in this product for the same reason as in the interior wall paint. We also use base B1 in this product for the purposes of our tests.

The difference between the interior and exterior wall paints is in the volume of the resin in the recipe. Exterior wall paints have around 30 % of resin, this is necessary in order to protect (cover) the pigment and improve the light and weather fastness. Interior wall paints have less resin, around 20 %, and its volume is more connected to the washability of the paint. Another main difference between the exterior and interior color shades (wall paint) is in their pigment chemistry. The first have more organic pigments and the second more inorganic pigments. Inorganic pigments have better light and weather fastness.

Recipe for the decorative solventborne paint for metal consists of: resins, pigment, dispersing agent, fillers, solvent and defoamers. Resins are two: one is thixotropic with the function to prevent the sedimentation of the pigment, the other is a high solid long oil alkyd with solid content 75 % (ISO 976). With such a high solid content of the resin it is possible to produce products with lower VOC values. We have five bases in this product since a base without any pigment in this product results in a much worse opacity than waterborne paints. This is due to the fact that wall and façade paints are applied with a higher film thickness (200 microns and more) and metal (and wood) paints with a lower film thickness (60 microns and less). This variation is an outcome of the different application viscosity which is 8 Pas and more for wall paints and around 1 Pas for enamels.

The recipe for the decorative solventborne paint for wood consists of: resin, dispersing agent, solvent and defoamers. In this case we have a product with only one base called B3. This base is without any pigment. With this product which is used for wood we do not want to have colour shades which would have opacity. Therefore we make sure that we use colorants in minimum values especially when there is an option to use colorants with inorganic pigments. Since we know that with inorganic pigments we can have better opacity.

## **3.2. Measurements of main parameters in colorants**

Our focus was to measure the differences in rheological parameters in different storage conditions. When we saw that rheological parameters remained stable we proceeded with the testing of the colorants in the base paints and dispensers.

### **3.2.1. Rheology**

I want to divide this part into three sections: rheology, rheometry and viscoelasticity. These are the three main parts with which we can present their logical use and connection with paints and the paint industry.

#### **Rheology**

Rheology is a branch of physics (and physical chemistry) in which the most important variables come from the field of mechanics: forces, deflections and velocities. Rheology describes the deformation of a body under the influence of stresses. “Bodies” in this context can be solids, liquids or gases. It is the science of deformation and flow [4, 5].

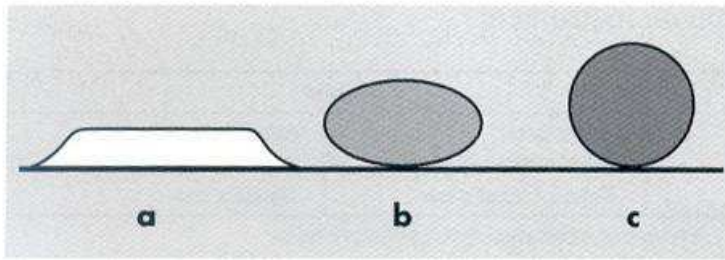
The term “rheology” originates from the Greek: “rheos” meaning “the river”, “flowing”, “streaming”. Thus, rheology is literally “flow science”. However, rheological experiments do not merely reveal information about the flow behaviour of liquids, but also the deformation behaviour of solids. The connection here is that large deformations produced by shear forces cause many materials to flow.

All forms of shear behaviour which can be theoretical described in a scientific way can be viewed as lying in between two extremes: the flow of ideal viscous liquids on one hand and the deformation of ideal elastic solids on the other.

The behaviour of all real materials is based on the combination of both the viscous and the elastic portion and therefore, it is called viscoelastic. A wallpaper paste is a viscoelastic liquid, for example, and a gum eraser is a viscoelastic solid.

Ideal solids deform elastically. The energy required for the deformation is fully recovered when the stresses are removed. Ideal fluids such as liquids and gases deform irreversibly – they flow. The energy required for the deformation is

dissipated within the fluid in the form of heat and cannot be recovered simply by removing the stresses.



**Figure 2:** Deformation behaviour after hitting the floor: a) mineral oil, b) plasticine, c) steel ball [4].

Rheology measurements can be done with every material by using either Newton's law or Hook's law. Both describe different materials: Newton ideal fluids, Hook ideal solids. The combination of both laws can describe the materials which are between the ideal fluid and the ideal solid. For viscoelastic solids Hook's component is dominant and in case of viscoelastic fluids Newton's component is dominant.

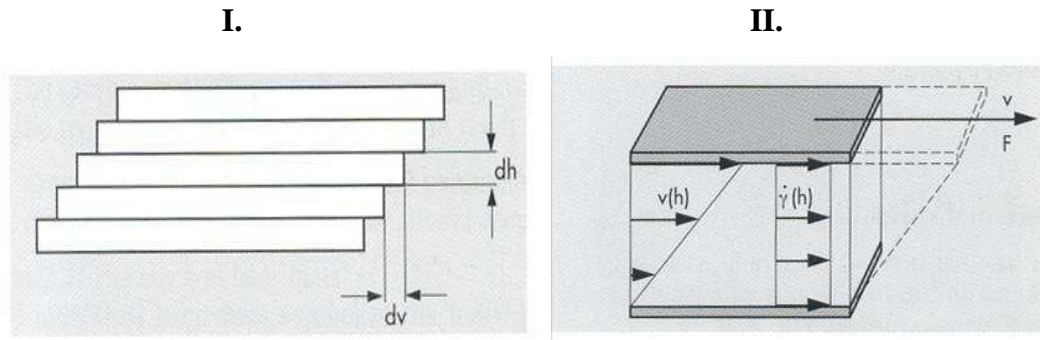
In coatings Newton's component is dominant which means that coatings are viscoelastic fluids.

### **Rheometry**

Measuring technology used to determinate rheological data is called rheometry. The measurement of the viscosity of liquids first requires the definition of the parameters which are involved in the flow. Then one has to find suitable test conditions which enable the flow properties to be objective and reproducible. Isaac Newton was the first to come up with the basic law of viscosimetry describing the flow behaviour of an ideal liquid:

$$\tau = \eta * \dot{\gamma}$$

**Equation 2:** Shear stress = viscosity \* shear rate [4].



**Figure 3:** I.) flowing layers, which in laminar flow has the same h-thickness. II.) connection between velocity and shear rate (also in the shear gap of rheometer Figure 5 and Figure 14) [4].

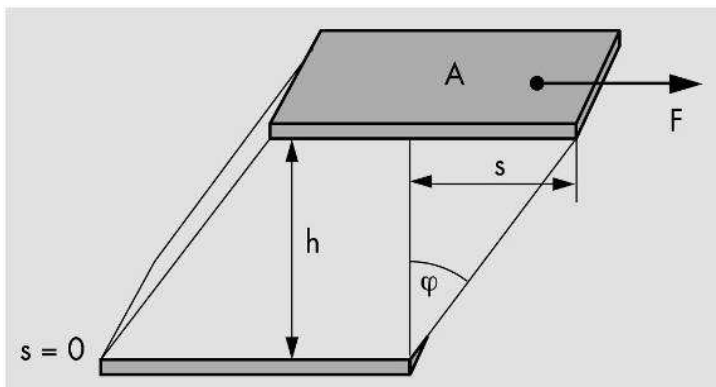
For the laminar, idealviscous flow, the difference in velocity between neighbouring layers is the same value ( $dv = \text{const}$ ) since the velocity  $v(h)$  decreases linearly in the gap between the plates. All layers are assumed to have the same thickness ( $dh = \text{const}$ ). Therefore, it follows that the shear rate  $\dot{\gamma}$  is constant for every point between the plates because:  $\dot{\gamma} = dv/dh = \text{const}/\text{const} = \text{const}$  (Figure 3).

Shear stress =  $\tau$

A force  $F$  applied tangentially to an area  $A$  being the interface between the upper plate and the liquid underneath, leads to a flow in the liquid layer. The velocity of flow that can be maintained for a given force is controlled by the internal resistance of liquid, i.e. by its viscosity.

$$\tau = F/A$$

**Equation 3:**  $\tau$ (shear stress) =  $F$ (force)/ $A$  (area) =  $N$ (Newton)/ $m^2$  = Pa [Pascal] [4].



**Figure 4:** Deformation of material in shear gap of the Two-Plate-Model [4].



In all fluids, there are frictional forces between the molecules and, therefore, they display a certain flow resistance which can be measured as viscosity. All materials which clearly show flow behaviour are referred to as fluids (this applies to liquids and gases)  $\eta = \tau / \dot{\gamma}$  (Equation 4).

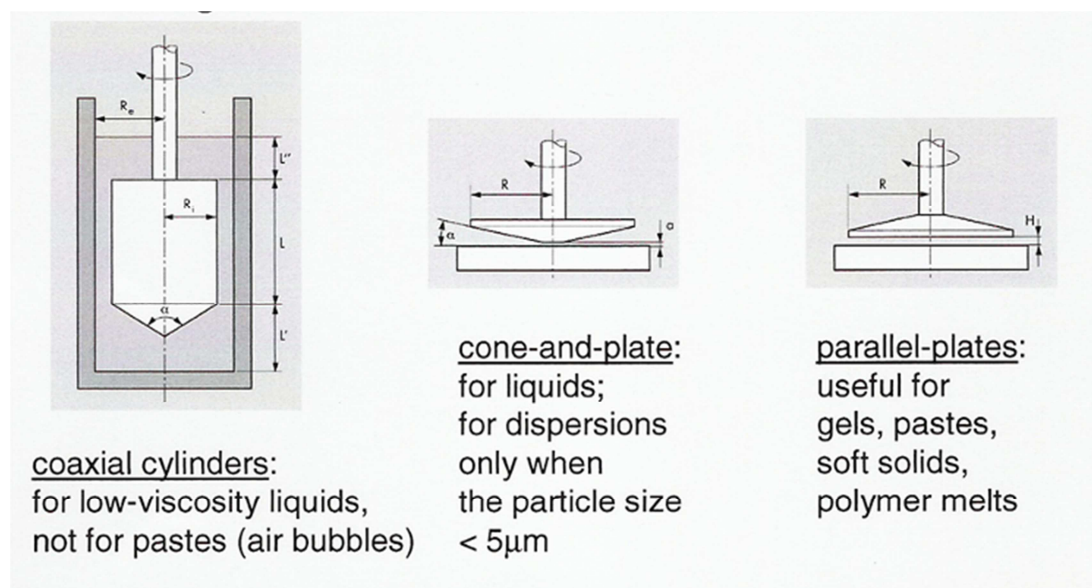
### Rheometer

A simple device measuring the viscosity function via speed (or shear rate) controlled rotational tests is usually called viscometer. Instruments which enable further rheological tests, such as torque (or shear stress) controlled rotational tests are referred to as rheometers. Many rheometers can also carry out other tests such as creep, relaxation and oscillatory tests.

Rotational test results in the rotational speed  $n$ , which is determined by the position sensor when the measured time is also taken into consideration. The shear rate is then calculated from  $n$ .

Creep test results in the time-dependent deflection or recovery angle. This method is mostly used to examine chemically unlinked and unfilled polymers in the form of melts and solutions, but is also suitable for determining the behaviour of chemically cross-linked polymers, gels and dispersions with a physical network of forces.

Oscillatory test is used to examine all kinds of viscoelastic materials, from low viscosity liquids, pastes, gels, polymer melts to elastomers and rigid solids, this kind of test is often referred to as dynamic mechanical analysis.



**Figure 5:** Three different types of sensor systems in the rheometer [6].

Rheometer can have different types of sensor systems which are seen in Figure 9. What type of sensor system we choose depends on the sample we want to measure.

### Classification of liquids

Before explaining the main characteristic of the viscoelastic flow behaviour let me first discuss the classification of liquids.

Liquids can be put into two groups:

- Newtonian liquids
- Non-Newtonian liquids

### Newtonian liquids

Ideal-viscous (or Newtonian) flow behaviour is formally described using Newton's law ( $\tau = \eta * \dot{\gamma}$ ). Isaac S. Newton recognized: The shear force acting (via the shear area) on a liquid proportional to the resulting flow velocity. The shear viscosity of a Newtonian fluid is independent of the degree or duration of the shear load [7].

Ideal-viscous materials are low molecular liquids such as water, solvents, mineral oils (without polymer additives), standard oils, pure and clean bitumen and blood plasma.

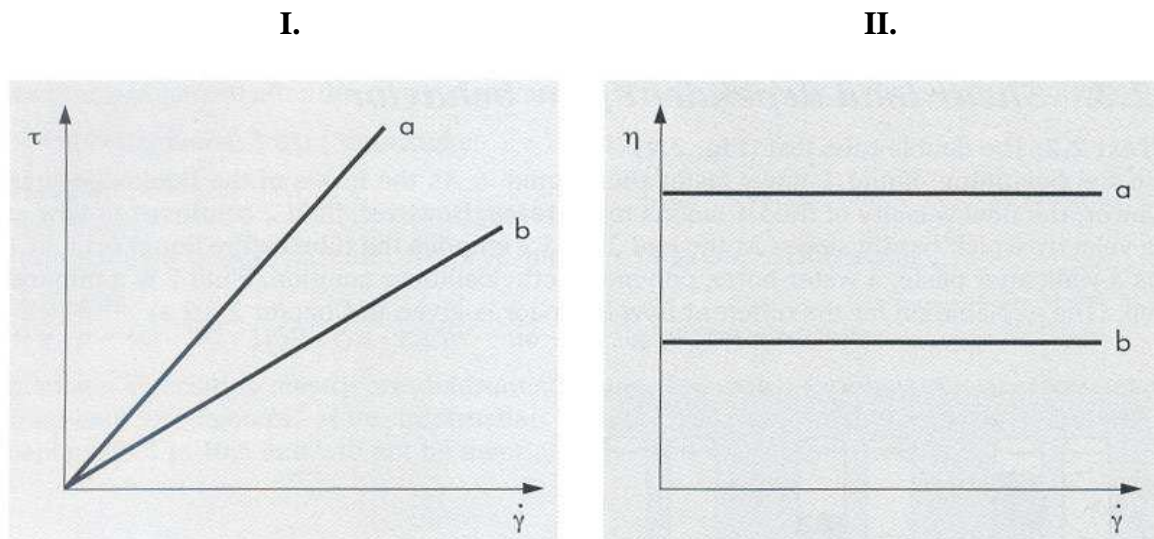


Figure 6: I.) flow curves and II.) viscosity curves of two ideal-viscous fluids [4].

Figure 6 shows the correlation between  $\tau$  and  $\dot{\gamma}$  from both graphs, we can see the behaviour of ideal-viscous fluids which depends on  $\dot{\gamma}$ .

## Non-Newtonian liquids

The other liquids which are not exhibiting this ideal flow behaviour are called `Non-Newtonian Liquids. We can classify liquids on the basis of the rheological behaviour.

Shear load dependent flow behaviour:

- pseudoplastic or shear-thinning flow behaviour,
- dilatant or shear-thickening flow behaviour,
- plastic flow behaviour,

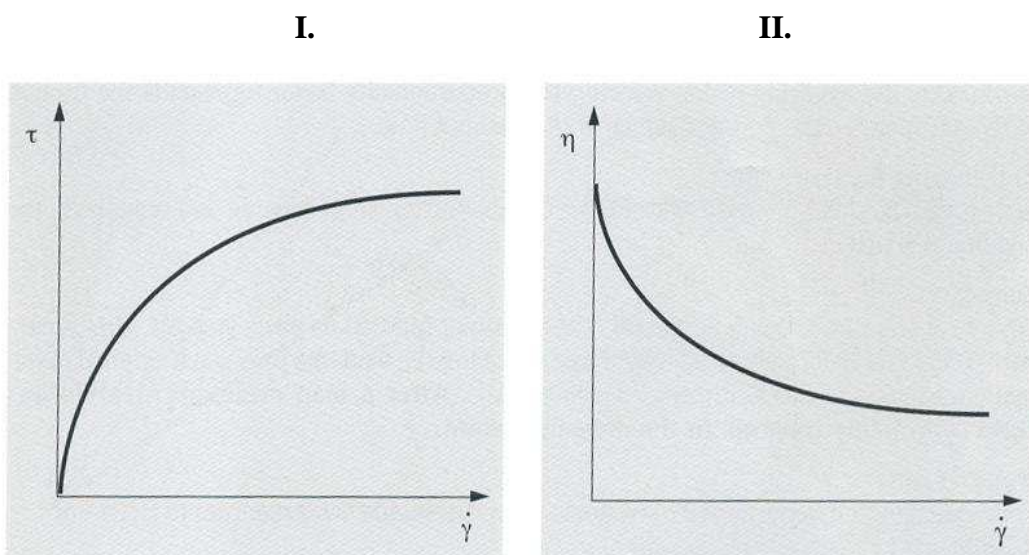
Time dependent flow behaviour:

- thixotropy,
- rheopectic, anti-thixotropic flow behaviour,
- viscoelastic behaviour.

There are also materials in which the flow behaviour depends on temperature and pressure.

### Pseudoplastic flow behaviour

The viscosity for samples that display shear-thinning flow behaviour depends on the degree of the shear load. The curve in Figure 7 is decreasing; the viscosity decreases with the increasing load.



**Figure 7:** I.) flow curve and II.) viscosity curve [4].

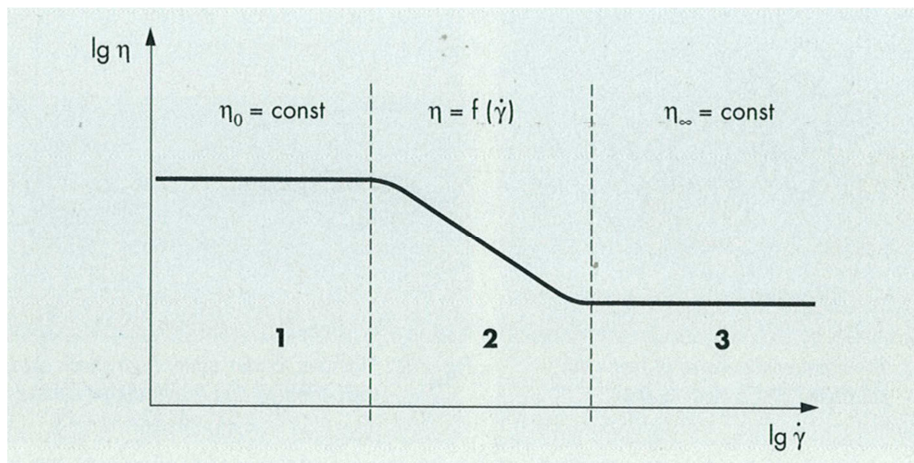
Pseudoplastic flow behaviour liquids make an inside structure, which forms because of Van der Waals electrostatic and Brown's force between crystals and other small parts in the liquids.

The force of the shear stress viscosity drops with a higher shear rate. This happens because the structure of material breaks. Figure 8 shows the viscosity curve of a polymer. As it can be seen the curve is separated in three ranges.

The first is Newtonian range with the plateau value of the zero-shear viscosity  $\eta_0$ .

The second range shows the dropping of viscosity  $\eta$  with increasing of the shear rate.

The third range shows the second Newtonian range with the plateau of the infinite-shear viscosity  $\eta_\infty$ .



**Figure 8:** Viscosity in pseudoplastic material by increasing the shear rate [4].

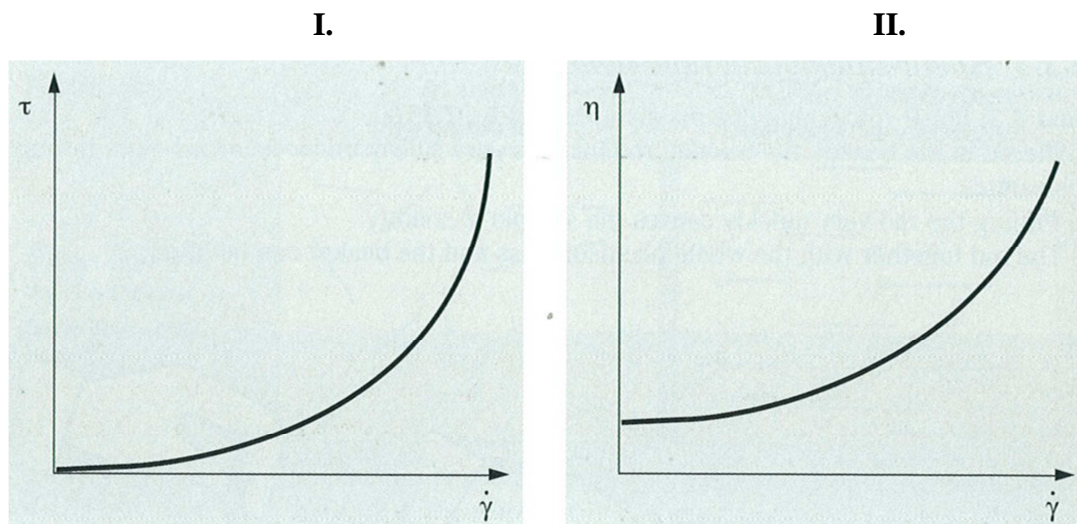
The pseudoplastic flow behaviour is present in materials like paints, glues, polymer solutions, polymer melts, shampoos, etc.

### **Dilatant flow behaviour**

Structures in polymers with the shear-thickening flow behaviour: The dilatant flow behaviour occurs in concentrated chemically unlinked polymers due to mechanical entanglements between the mostly branched molecule chains. The higher the shear load the more the molecule chains prevent each other from moving.

Structures in dispersions with the shear-thickening flow behaviour: if, during the shearing process with highly concentrated suspensions the particles touch each other more and more (they may even become wedged together), the consequences are similar, the resistance to flow increases. The shape of the particles is also important.

Cube-shaped particles take up more volume when rotating than at rest. As a consequence, there is less free volume between the particles for the dispersing liquid. On the other hand, spherical particles take up the same amount of volume when rotating as when at rest; those dispersions are less likely to show dilatance. A material's ability to flow can be improved by increasing the amount of free volume available between the particles. This can be achieved by changing the shape of the particles (and of course also by adding extra liquid).

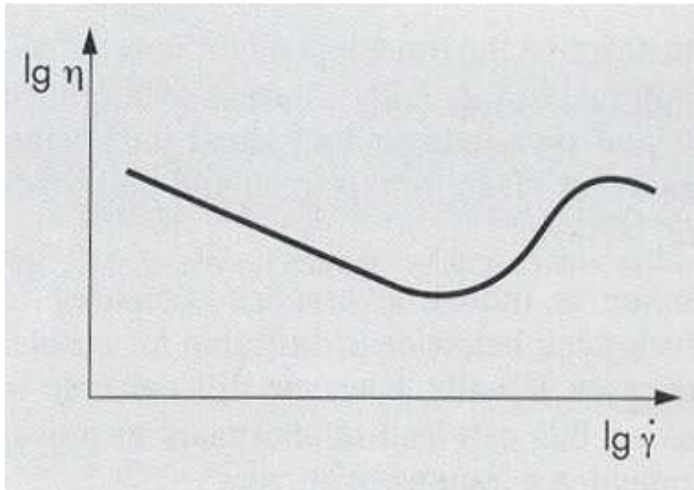


**Figure 9:** I.) flow curve of dilatant material and II.) viscosity curve of dilatant material [4].

As it is seen from Figure 9 the viscosity is increasing by increasing the shear rate. This behaviour is undesirable and it should never be ignored because it can lead to enormous technical problems. We are trying to avoid the dilatant flow behaviour in paint industry.

In some cases (samples) the dilatant flow behaviour can be noticed in some areas of shear rate, sometimes in a higher shear rate. It is therefore important that the measurements are made properly. A sample of the dilatant peak can be seen in Figure 14.



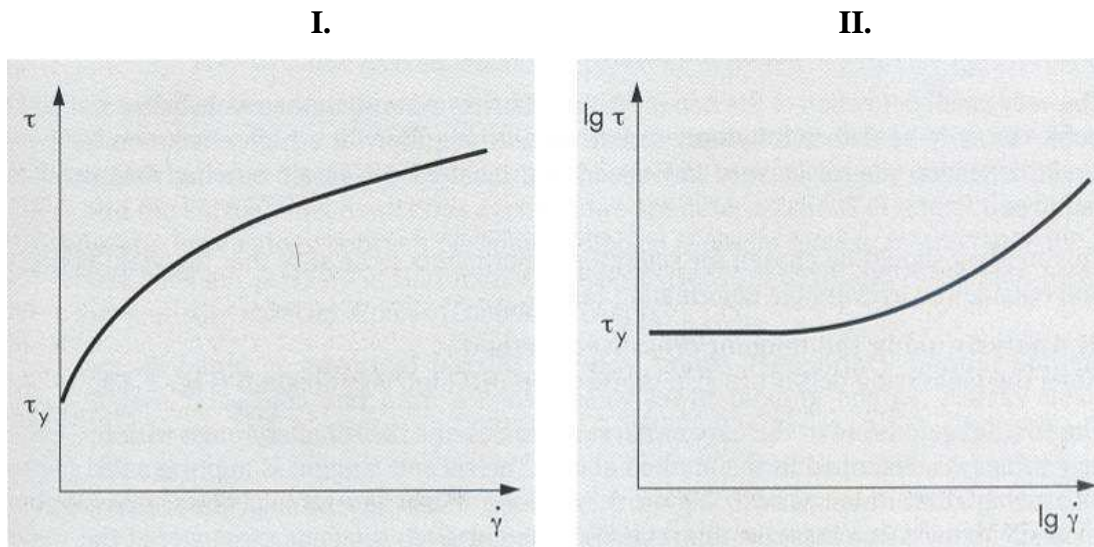


**Figure 10:** Viscosity curve of a shear-thickening material, showing a dilatant peak [4].

Examples of dilatant flow behaviour materials are dispersions with a high concentration of solids or polymers; such as ceramic suspensions, starch dispersions, plastisol pastes.

### **Plastic flow behaviour**

Liquids with plastic flow behaviour require a certain shear force to flow. The structure of such liquids is strong enough that it does not break down; it only shows a plastic deformation. When the shear stress is strong enough in the liquid, that the particles which create the structure start moving, this also forces the liquid to flow. The shear stress where the liquid starts moving their particles is called yield stress ( $\tau_0/\text{Pa}$ ). The values of yield stress are difficult to measure. The value of the apparent yield point depends on the speed resolution of a rheometer. The yield point is the one shear stress value at which the range of reversible elastic deformation ends and the range of irreversible deformation or viscoelastic/viscous flow begins.

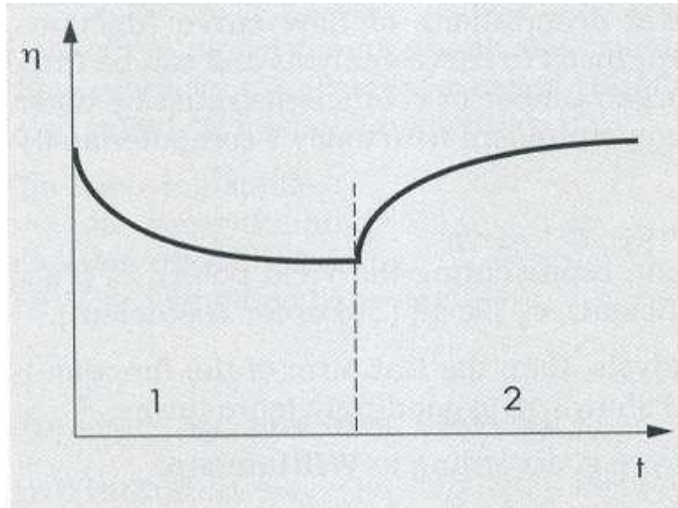


**Figure 11:** I.) flow curve with a yield point and II.) flow curve with a yield point [4].

Examples of materials with a yield point are dispersions with a high concentration of solids and gels (e.g. plastisol pastes, conductor pastes, ketchup, mayonnaise, toothpastes, dispersion paints, printing pastes, ceramic masses, lipstick, creams, chocolate melts, yogurt, butter, etc.) [4, 8].

### **Thixotropic flow behaviour**

Time dependent flow behaviour is the thixotropic behaviour which means a reduction in structural strength during the shear load phase and the more or less rapid, but complete structural regeneration during the subsequent rest phase. As it can be seen from Figure 12 viscosity is dropping by constant shear rate depending on the time. The structure is created again when the shear rate is removed.



**Figure 12:** Viscosity curve of a thixotropic material [4].

*(1) time-dependent structural decomposition under constantly high shear load*

*(2) time-dependent structural regeneration when at rest*

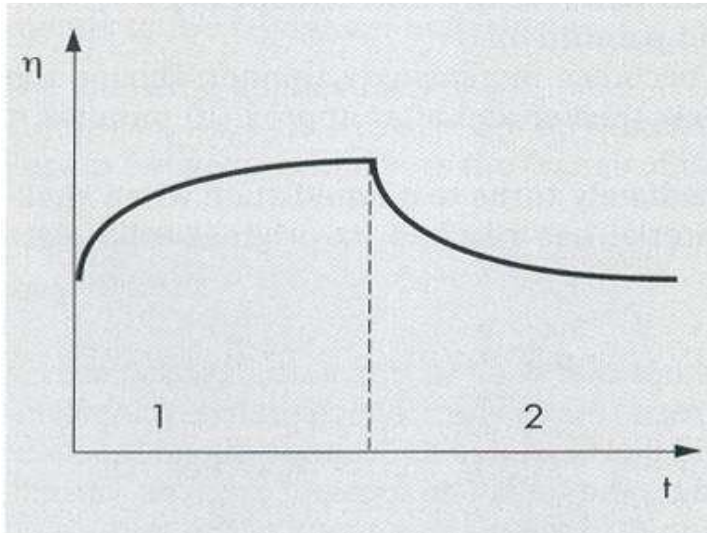
Examples of thixotropic materials are almost all dispersions (suspensions, emulsions, foams), such as pastes, creams, ketchup, printing inks and gels.

### **Rheopectic (anti-thixotropic) flow behaviour**

Rheopectic behaviour means an increase in the structural strength during the load phase and a more or less rapid but complete decomposition of the increased structural strength during the subsequent period of rest. Rheopexy is sometimes called `anti-thixotropy` or `negative thixotropy`. This increase/decrease cycle in structural strength is a completely reversible process.

Rheopectic behaviour is defined as a time-dependent behaviour. A material that displays the rheopectic behaviour tends not to flow homogeneously. Wall slipping effects and separation should always be expected. The rheopectic behaviour is much less common than the thixotropic behaviour.





**Figure 13:** Viscosity curve of a rheopectic material [4].

Examples of rheopectic materials are dispersions with a high concentration of solids (e.g. latex dispersions, casting slips or plastisols). We are trying to avoid the rheopectic flow behaviour in paint industry.

### **Viscoelastic behaviour**

A viscoelastic material always shows viscous and elastic behaviours. The viscous part behaves according to Newton's law, and the elastic part behaves according to Hook's law. Depending on their rheological behaviour viscoelastic liquids differ from viscoelastic solids. Viscoelastic materials always show a delayed response when load is applied and removed.

Viscoelastic liquids are a combination of Hook's law and Newton's law where Newton's component is predominating. Therefore, the material behaves as a liquid with viscoelastic characteristics.

Viscoelastic solids are a combination of Hook's law and Newton's law where Hook's component is predominating. Therefore, the material behaves as a solid with viscoelastic character.

More or less coatings are liquids with the viscoelastic flow behaviour. Different materials which are viscoelastic liquids can show pseudoplastic, dilatant, plastic, thixotropy, rheopectic or anti-thixotropic flow behaviours. For materials like decorative coatings we do not want to have dilatant and rheopectic flow behaviours. Every other rheology behaviour in coatings is useful in different application surfaces. For instance the pseudoplastic flow (time independent) behaviour is useful when

putting a coating on a surface with the use of a spraying technic. With this we want to avoid flowing of the coating from the surface. Also the thixotropic flow behaviour is useful to avoid sedimentation of the pigment. When we use brush or roller, we want to have a coating with the thixotropic flow (time dependent) behaviour. At the same time the coating must not create the structure too fast in order to give a result of good levelling on the surface. This is to avoid marks from the brush and roller when the coating gets dry [4, 9, 10].

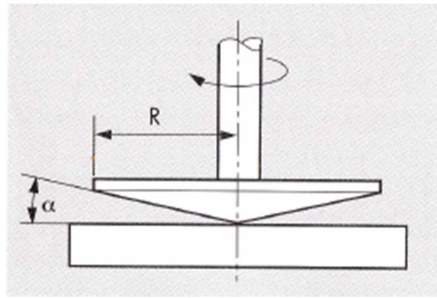
### ***3.2.1.1. Rheology measurements***

When a new paint is made it is important to use all the tests which can help us finish our work in the expected way. Rheology describes the deformation of a subject (in our case liquid) under the influence of shear forces [2]. Rheometry is the measuring technology used to determinate rheological data  $\eta$  - viscosity,  $G'$  - storage modulus,  $G''$  - loss modulus. The measurement of the viscosity of liquids first requires the definition of the parameters which are involved in the flow [4, 9].

For laminar, ideal viscous flow the difference in velocity between neighboring layers is the same ( $dv = \text{const}$ ) since the velocity  $v$  ( $h$  - thickness) decreases linearly in the gap between the plates in rheometer (Figure 14). All layers are assumed to have the same thickness ( $dh = \text{const}$ ) (Figure 3). Therefore, it follows that the shear rate  $\dot{\gamma}$  is constant for every point between the plates because:  $\dot{\gamma} = dv/dh = \text{const}$ .

Both  $\dot{\gamma}$  and  $v$  provide information about the velocity of the flowing fluid and the advancing of it. The advantage of the shear rate is that it shows a constant value throughout the shear gap, which is therefore independent of the position of the flowing layer.

In all fluids, there are frictional forces between the molecules and, therefore, they display a certain flow resistance which can be measured as viscosity. We would like to explain the rheology parameters of the paint that can be determined by rheology flow graph and the behavioral characteristics seen during the application of the paint. We saw that rheology flow test is the only test needed for our samples. The main rheology tests are: temperature test, frequency sweep test and flow test.



**Figure 14:** The main part of a rheometer. The bottom plate is fixed and in the middle connected with a cone-shaped plate. The sample is placed into the gap between the plates. The cone-shaped plate is turning with shear rate, which is changed from  $0.01 \text{ s}^{-1}$  to  $1000 \text{ s}^{-1}$  depending on the test. [4]

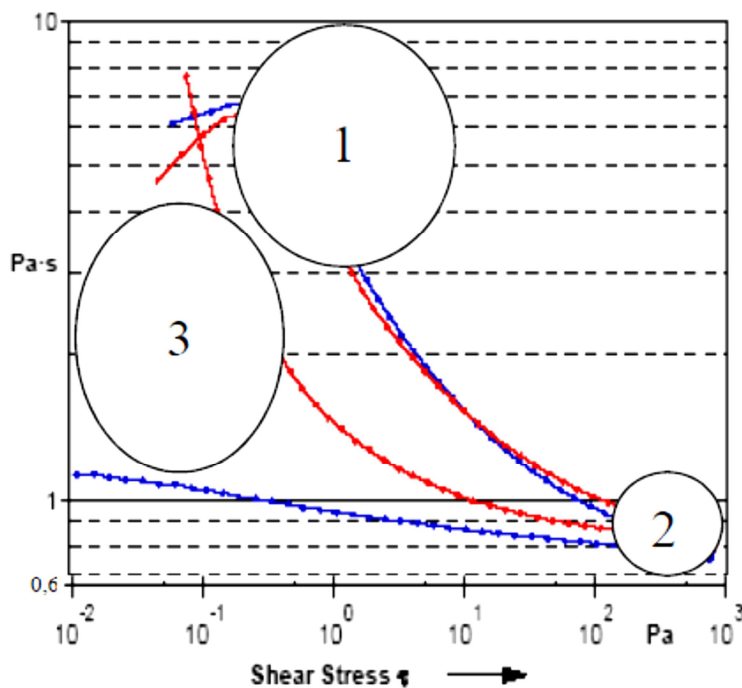
All measurements were done using a rheometer (its producer is Anton Paar, Figure 15) by cone-and-plate measuring system (Figure 14). Several measuring systems are available for determining paint properties: Coaxial cylinder, Double-gap, Parallel-plate, Mooney/Ewart measuring systems. For our samples it was enough to use a cone and plate system which was standardized in 1976 as DIN 53018 and adopted more or less completely in 1993 as ISO 3219 [4, 11].



**Figure 15:** Anton Paar rheometer [12].

### 3.2.1.2. Flow test

The test describes the use of paints in practice. It starts with a low shear rate (velocity) and then grows to the maximum value. When the shear rate grows, the viscosity drops and that is comparable with the drop of the viscosity when the paint is applied with a brush. Flow curve is formed in 3 steps. In step no. 1 (Figure 16) shear rate  $\dot{\gamma}$  rises from  $0.01 \text{ s}^{-1}$  to  $1000 \text{ s}^{-1}$  with 40 points in 348 seconds. Step no. 2 describes  $\dot{\gamma}$  with constant shear rate  $1000 \text{ s}^{-1}$  with 2 points in 30 seconds. Step no. 3 describes the decrease in shear rate  $\dot{\gamma}$  from  $1000 \text{ s}^{-1}$  to  $0.01 \text{ s}^{-1}$  with 40 points in 207 seconds.



**Figure 16:** This figure shows a measurement performed during the time when the shear stress is increasing. It indicates how this affects viscosity of the samples. The figure of flow curve also shows what effects decreases in the shear stress have on viscosity. Numbers 1, 2 and 3 show the areas. Number 1 introduces the area showing the structure of the measured sample. Number 2 introduces the area of shear stress application. Number 3 introduces the area indicating the behavior of the sample after removing the shear stress.

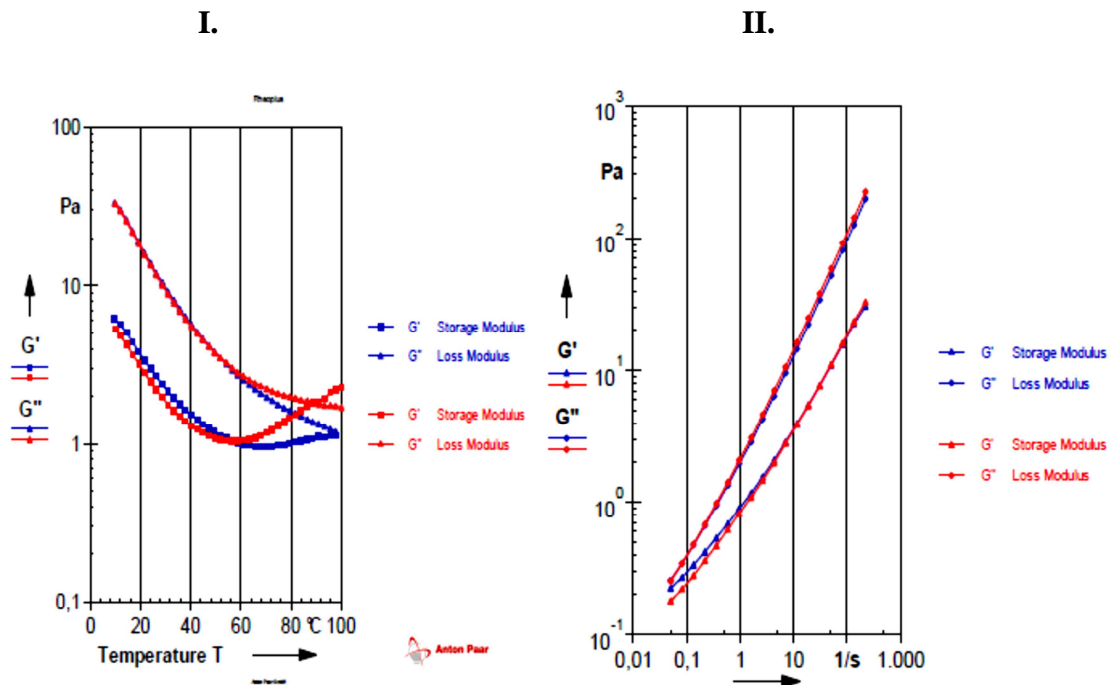
The flow test describes the use of paint in practice. It starts with a low shear rate (velocity) and then grows to the maximum value. During stirring a coating or colorant with a stick shear rate grows and the viscosity normally drops. This can be compared with rheology flow graph after the shear rate drops we can measure how viscosity increases (structure of the paint is forming back).

### 3.2.1.3. Temperature test

Changes in the system caused by warming up the sample were measured by this test. The best sample is the one, whose viscosity or other rheological parameters ( $G'$ - storage modulus,  $G''$ - loss modulus) do not increase with temperature. This test is a type of oscillatory test where frequency (1.6 Hz) and deformation ( $\gamma = 2\%$ ) are constant. Temperature increases from 10°C to 100°C at the rate of 6.75°C/min. The test lasts 800 seconds and it measures 40 points (Figure 17).

### 3.2.1.4. Frequency sweep test

This test shows what can happen with a sample in the future by storage. It shows whether the pigment in the sample will settle down. It is not possible to predict the time of sedimentation, but it is possible to predict which sample will sediment before another. The test is done in LVE area with a constant deformation ( $\gamma = 2\%$ ) and changing frequency from 95 Hz to 0.008 Hz. The test describes by very low frequency if the sample has a gel structure  $G' > G''$  or not. An example of the frequency sweep test graph is shown in Figure 17 on the right.



**Figure 17:** I.) temperature tests with  $G'$  and  $G''$  values of red and blue samples, which are heated up to 100°C. II.) frequency sweep test with  $G'$  and  $G''$  values of the red and blue samples, when different frequency is applied.

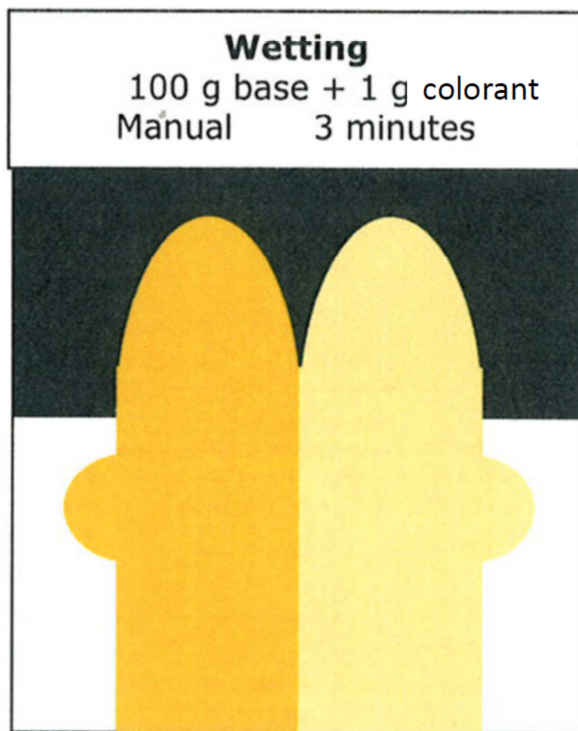
Temperature test (Figure 17) shows the dependence of the sample's behavior on the changes in temperature. In Figure 17,  $G'$  starts increasing when temperature is  $55^{\circ}\text{C}$  that is for the red sample. The  $G'$  from the blue sample does not increase so much with a higher temperature as is the case with the red sample. The results of temperature test show that interactions between particles are stronger in the red sample. This accelerated test for paints can be correlated according to the paint properties after long periods of time (flocculation of the pigment after long time). This is also confirmed with the flow test (Figure 16) where number 3 shows differences among samples in that area. This connection between the three methods is not always true (not for all liquids) but it turns out that it can be applied for our samples.

Rheology testing of the products is important when rheology influences the main property of the product - which is the case with paints. Flow test graphs help us obtain results faster. It was determined that the only test which is needed to obtain the rheology properties (for our samples) is the rheology flow test. The rheology flow test shows the behavior of a paint when it is used on a surface. It also shows stability which is normally seen in other tests (temperature test, frequency sweep test). A problem with sedimentation can be seen using the frequency sweep test but this test was not needed for our samples since results of the frequency sweep test were predicted in the flow test. The rheology flow test graph also explains interactions between particles of the pigment and the stability of the sample; that is with values of viscosity when shear stress drops. Stability of the system can also be measured with the temperature test. However, it was not required for our samples, since the stability could be determined with the flow test. We took advantage of that fact whenever working with more or less the same raw materials and just in different volumes. Our results will enable a faster and more precise determination of rheology properties.

### **3.3. Wetting test**

The testing is done to see if the paint is sufficiently wetted to meet the demands of the tinting system. If the paint has a wetting problem with the colorants, it means that insufficient surfactant is available to wet all the free surfaces on the titanium dioxide

in the paint. This means that an addition of surfactant is necessary. Usually a combination of an anionic and a non-ionic works best to assure a good wetting of the paint and the colorant. This does not mean that the base paint is not sufficiently wetted as a white, but when colorants are added and stirred in strongly, the surfactants of the colorant migrate to the titanium dioxide or filler particles of the paint and the colorant's pigment particles re-agglomerate. The colorant will therefore not reach its full color strength.



**Figure 18:** Example of poorly wetted paint [13].

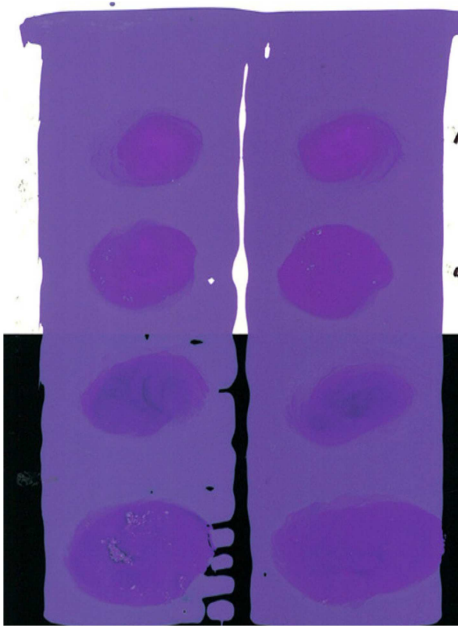
Figure 18 shows the difference in wetting. The right shade shows a sample which was being mixed for 3 minutes in a shaker and on the left is a sample mixed by a stick with controlled care. But since shakers are used in the market for such cases we must improve our wetting characteristics between the colorant and the base paint. The important thing is that we get as much color strength from the pigment as possible.

We were testing the colorants only with shakers we were mixing for 3 and 10 minutes and we were checking the differences in wetting among samples after these samples have been shaken for 3 and 10 minutes. Sometimes samples needed more than 3 minutes to be shaken suitably. If a difference is noticed in the colour strength

between a sample which has been shaken for 3 minutes and the one shaken for 10 minutes then some work is still required for the optimization of a colorant or base paint.

### 3.3.1. Compatibility in base paint

Incompatibility is used as a term to indicate different types of problems: loss in gloss level, extended drying time or loss of certain flow characteristics of a paint. Compatibility referred to the color development of a colorant in paint is called color acceptance. This means that the colorant cannot develop its full color strength in paint.



**Figure 19:** Example of bad compatibility.

### 3.3.2. Colorants compatibility

It is also important that the colorants that are mixed together do not show any compatibility problems since they are often together in colour shades. To diminish this problem we should avoid using different raw materials; this means that we use a different dispersing agent or any other raw material only when necessary.



Colorimetric measurements (in sections 4.2. and 4.3.) were done using spectrophotometer Datacolor Spectraflash SF 600 PLUS (Figure 20). The instrument can work with different programs and the results can be read from the computer. Values obtained from the spectrophotometer are CIEL\*a\*b\* colour differences.



**Figure 20:** Equipment (Datacolor Spectraflash SF 600 PLUS) for measuring CIEL\*a\*b\* colour differences.

### 3.4. FTIR Spectroscopy

FTIR – Fourier Transform Infrared. Infrared spectroscopy is an important technique in organic chemistry. It is an easy way to identify the presence of certain functional groups in a molecule. Also, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities [14].

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore,

infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis [14, 15].

FTIR spectroscopy was used in order to detect a possible chemical reaction between colorants and products (basses) components.

In our measurements we used FTIR NEXUS instrument, by Thermo Nicolet. For recording FTIR spectra in solventborne samples we used KBr-crystal in the spectral range from 400 to 4000  $\text{cm}^{-1}$  with resolution 4  $\text{cm}^{-1}$ . For recording waterborne samples we used ZnSe-crystal in the range from 750 to 4000  $\text{cm}^{-1}$  with resolution 4  $\text{cm}^{-1}$ . Samples were put on the KBr or ZnSe crystals in the form of a thin film.

### 3.5. Differential scanning calorimetry

Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

The technique was developed by E.S. Watson and M.J. O'Neill in 1962 [16].

The result of a DSC experiment is a curve of heat flux versus temperature or versus time. There are two different conventions: exothermic reactions in the sample shown with a positive or negative peak, depending on the kind of technology used in the experiment. This curve can be used to calculate enthalpies of transitions. This is done by integrating the peak corresponding to a given transition. It can be shown that the enthalpy of transition can be expressed using the following equation:

$$\Delta H = KA$$

**Equation 4: Formula enthalpy of transition [17].**

Where  $\Delta H$  is the enthalpy of transition,  $K$  is the calorimetric constant, and  $A$  is the area under the curve. The calorimetric constant will vary from instrument to instrument, and can be determined by analyzing a well-characterized sample with known enthalpies of transition [17].

This test method consists of heating or cooling the test material at a controlled rate under specified purge gas at a controlled flow rate and continuously monitoring with a suitable sensing device the difference in heat input between a reference material and a test material due to energy changes in the material. A transition is marked by absorption or release of energy by the specimen resulting in a corresponding endothermic or exothermic peak or base line shift in the heating or cooling curve. Areas under the crystallization exotherm or fusion endotherm of the test materials are compared against the respective areas obtained by the treatment of a well-characterized standard [18].

We measured two bases: waterborne interior wall paint and solventborne paint for metal. We also measured only the colorant. Afterwards we measured interior wall paint mixed with 5 % of violet universal colorant and the paint for metal mixed with 10 % of violet universal colorant.

The same test was carried out for all the samples. We were monitoring the samples at 25°C for 180 minutes. Then we started rising the temperature for 5°C/minute up to 40°C. At temperature 40°C we measured the samples for another 20 minutes.

With this method we wanted to check if there was any chemical reaction between the base paints and the colorant. The goal was the same as with FTIR spectroscopy but since the differential scanning calorimetry is more precise we decided to check our samples with this method as well. We were looking for a peak in the graph which indicates a difference in energy and means that a chemical reaction has occurred.

### **3.6. Measurement of volatile organic compounds**

The method is based on ISO 11890-2:2007 part 2 and is known as gas-chromatographic method.

It specifies a method for the determination of volatile organic compound (VOC) content of paints, varnishes and their raw materials. This part is preferred if the

expected VOC content is greater than 0.1 % by mass and less than about 15.0 % by mass. When the VOC content is greater than about 15.0 % by mass, the less complicated method given in ISO 11890-1 may be used [1, 19].

Sample preparation for measurement:

0,5 g of our sample (colorant) was prepared together with 5,0 g of methanol and 4 $\mu$ L of internal standard methylisobutylketone. A sample prepared in this way required 5 minutes of mixing.

Gas-chromatic conditions on which we performed measurements:

- Injector temperature was 200°C (i.e. the place before the column).
- The stove was heated 1 min/40°C, than 10°C/minute to 250°C and 1 minute/250°C.
- Column length was 25 m with internal diameter 0,2 mm.
- Detector was heated on 280°C in order to avoid the condensation.

Detached peaks were determined qualitatively with chromatograph program.

Method lasted 18 minute for each sample.

### **3.7. Dispenser**

To ensure a good stability of a colorant we have to know where it will be used and in what conditions. We generally have to include: transport conditions, storage conditions and conditions in a dispenser. Transport and storage conditions were tested by placing the samples into a stove (40°C) and checking the changes on rheological parameters. The conditions which colorants undergo in dispensers were also achieved using a dispensing machine.

Dispensers are machines used to storage and dispense colorants at a certain time. Machines in the tinting system are industrial and decorative. The differences between the two of them are in their pump technology, speed and therefore also in price. Pump technology can be piston pump, below pump or gear pump. In the decorative tinting system a piston pump and below pump are employed. Those two technologies are more acceptable for decorative colorants from the point of view of costs. Decorative dispensers are not exposed to aggressive solventborne colorants and therefore the material from which these dispensers are made (pump, pipes) can be plastic or from any other low cost material. Industrial dispensers are exposed to

aggressive solvents and larger volumes which have to be dispensed in a short time. That is why industrial dispensers are made of more expensive materials.

The testing of the colorants was performed on a dispenser with a below pump technology. We decided to test on such a dispenser because it is of medium quality in comparison with those that can be found in the market for decorative colorants.



**Figure 21:** Dispenser for colorants [20].

We tested the behavior of the colorants in the dispenser in normal conditions which have to be ensured also in the market; i.e. with a room having a temperature in the range from 15°C to 25°C. Every dispenser has canisters where we put the colorants. The difference between the canisters is mainly in their volumes which vary from 1.5 to 5.0 liters - that is for decorative dispensers. Industrial dispensers normally have much bigger volumes. Every canister has a mixing system which prevents the sedimentation of the colorant. The purpose of our tests on the dispensers was to simulate possible conditions and usual use.

### **3.8. Raw materials in colorants**

Raw materials in colorants are dispersing agent, wetting agent, resin, pigment, solvent (water, solvent or VOC-free solvent), fillers, defoamers and deaerators. We can divide colorants into two groups:

- colorants with resin and
- colorants without resin.

Normally colorants with resin are in use for industrial coatings and colorants without resin for decorative coatings. The reason for that is in different consumption, quality of dispersing machines, quality of the products and price of the product. Normally colorants which are made of resin are made for implant products.

Raw materials for universal colorants in this thesis are: dispersing agent, wetting agent, pigment, solvents (water or VOC-free solvents), fillers, defoamers and deaerators. Our goal was to prepare a colorant which would have well defined rheological properties and show good compatibility with solventborne as well as waterborne coatings.

#### **3.8.1. Dispersing agent and wetting agent**

For colorants which are made without resin it is important which dispersing and wetting agents are in use. Dispersing agent gives steric stability to the pigment. Wetting agent ensures electrostatic stability. It is always better to have also steric stability which is usually present in solventborne products.

Wetting agents and dispersing agents can be divided into two groups:

- Low-molecular (conventional) and
- High molecular (polymers).

Both types improve the wetting process. Conventional agents are described according to their chemical structure. Therefore we know cationic, anionic, electro-neutral and anionic conventional agents.

The biggest differences between polymeric and conventional agents are in their chemical structure, molecule weight and principle of activity. High molecular polymers are more in use because they improve the stability in more aspects. These types of agents have active groups which can absorb organic surfaces (C, H, N, O

atoms) as well as inorganic surfaces. It is different for conventional agents: they usually have only one active group. Stability is connected to the price area, usually there is “a linear” explanation. The higher the price of the dispersing agent the longer the chain in polymer and the easier it is to achieve good stability.

Producers of wetting and dispersing agents often offer the wetting and dispersing properties in one product. In our tests we used three wetting and dispersing agents and two different dispersing agents.

Technical data in the section below are from the producer of those raw materials.

### **Wetting and dispersing agent 1**

Wetting and dispersing agent 1 has excellent pigment wetting properties for coatings and aqueous pigment pastes. Recommended use in aqueous, binder and solvent-free pigment pastes provides outstanding flow properties even at high pigment load.

Composition:

Mono functional oleo alkyleneoxide block copolymer.

Specification:

pH value 6.0 – 7.5 (10 % in water QC 2064.0)

Cloud point 61 – 65°C (QC 2062.0)

Water content 19 – 21 % (K. Fischer QP 1274.0)

Appearance – viscous liquid.

Density at 20°C approximately 1.03 g/cm<sup>3</sup> (DIN 51757)

Active content approximately 80 %

It can be used in water based alkyds, polyester resins as well as in aqueous polyurethane emulsions. Typical dosage for wetting and dispersing agent 1 in top-coats lies between 0.2 % and 1.5 % and should be added to the paint before grinding. The dosage used in pigment pastes depends on the actual pigments. Typical recommended addition levels for pigment pastes, calculated on the weight of pigments are as follows:

- Inorganic pigments 1 to 5 %.
- Organic pigments 10 to 30 %.
- Carbon black up to 50 %.

Product is durable for at least 2 years.

## **Dispersing agent 2**

Is a dispersing agent for aqueous binder free pigment pastes, especially for:

- Inorganic pigments in combination with non-ionic dispersing agents, like wetting and dispersing agent 1
- For universal pigment pastes (also suitable for solvent based coatings)

Dispersing agent 2 is a complex phosphoric acid ester of a non-ionic surfactant of the polyglycol ether type. The product is available as an approximately 30 % aqueous solution of the free phosphoric ester.

Specification:

- Appearance – clear viscous liquid.
- pH value 1.0 – 3.0 (10 % product) EN 1262.
- Analysis of dry residue is 29 to 31 % (QP2131.0)

It has an acid character. It stabilizes inorganic pigments by electrostatic repulsion. It can be used as the sole dispersing agent for the plaster slurries and also in combination with wetting and dispersing agent 1 to give a universal compatibility and colour acceptance even in solvent based coatings.

Dispersing agent 2 can be neutralised (salt) by using a weak or strong alkaline substance. Good test results have been achieved with aminomethylpropanol (Dispersing agent 4).

To achieve the best results dispersing agent 2 should be added to mill base and ground using effective dispersing equipment e.g. pearl-mill.

Typical recommended additional levels for pigment pastes, calculated on the weight of pigments are as follows:

- Titanium dioxide 2 to 5 %.
- Plaster, gypsum 2 to 3 %.
- Transparent iron oxide 15 to 25 %

Product is durable for at least 2 years.



### **Wetting and dispersing agent 3**

Wetting and dispersing agent 3 is especially designed for the production of aqueous, stable effect pigment gels. These can as well be produced with or without resin. It can be used for the treatment of organic and inorganic pigments. This leads to an easier and more stable incorporation of these pigments into aqueous pigments.

Composition of wetting and dispersing agent 3 is copolymers with pigment affinic groups.

Typical properties:

- Density at 20°C is 1.09 g/ml
- Active content approximately 98 %

Typical recommended additional levels for pigment pastes, calculated on the weight of pigments are as follows:

- Inorganic pigments 5 to 10 %.
- Titanium dioxide 4 to 7 %.
- Organic pigments 15 to 30 %.
- Carbon blacks 30 to 50 %.
- Effect pigments 3 to 5 %.

Product is durable for at least 2 years.

### **Dispersing agent 4**

Dispersing agent 4 use benefits include, but are not limited to, the following:

- Efficient amine for resin neutralization (high base strength, relatively low molecular weight)
- Acts as a Co-Dispersant for particulate systems
- Component of powerful anionic emulsifier systems
- Acts as a formaldehyde scavenger
- Corrosion inhibitor for steam-condensate lines
- Key component of metalworking fluids with extended fluid longevity
- Useful raw material for synthesis applications
- Multiple food contact approvals
- Use as a pigment dispersant at levels up to 0.25 % by weight of pigment

Composition of dispersing agent 4 is 2-Amino-2-methyl-1-propanol.

Typical properties:

- Density at 25°C is 0.949 g/ml
- Active content approximately 90 % solution
- pH of 0.1 M aqueous solution at 20°C is 11.3

Product is durable for at least 2 years.

### **Wetting and dispersing agent 5**

Wetting and dispersing agent 5 is primarily intended for aqueous systems. It is preferably used to stabilize organic pigments.

The composition of Wetting and dispersing agent 5 is a solution of high molecular weight block copolymers with pigment affinic groups.

Function of a wetting agent is to wet the pigment. The more the pigment is wetted the easier it is to ensure that a pigment stays well-dispersed.

Typical properties:

- Density at 20°C is 1.09 g/ml

Active content approximately 52 % .

Typical recommended additional levels for pigment pastes, calculated on the weight of pigments are as follows:

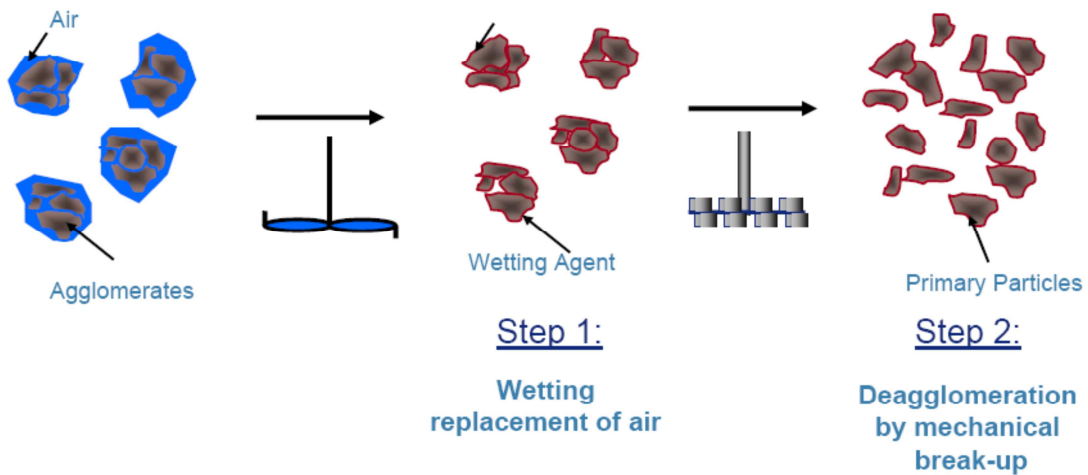
- Inorganic pigments 15 to 20 %.
- Titanium dioxide 4 to 6 %.
- Organic pigments 20 to 45 %.
- Carbon blacks 65 to 80 %.

Product is durable for at least 2 years.

The function of a dispersing agent is that it keeps pigment particles apart. It can do that if the surface of a pigment is well wetted. In order to obtain a stable colorant the right combination of wetting and dispersing agents has to be found and also in the right volume.

### 3.8.2. Pigment

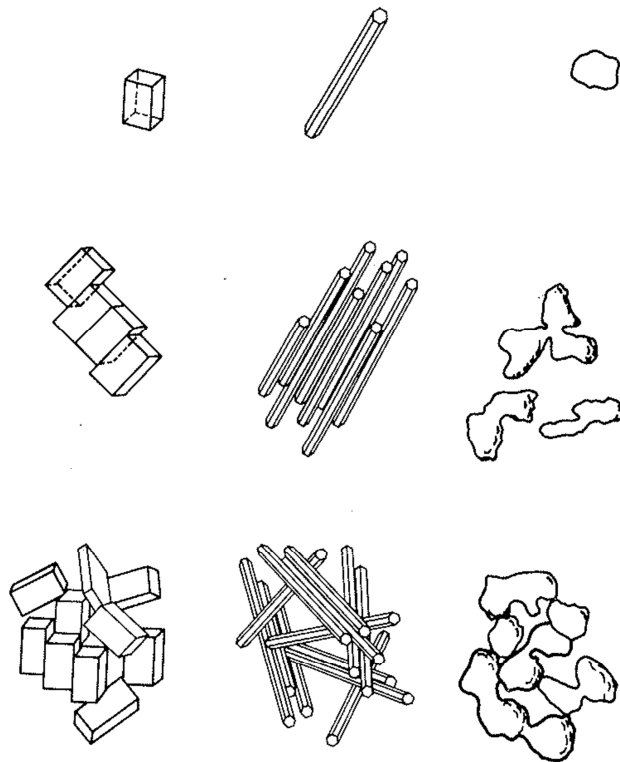
Pigment is a raw material to which every other raw material in recipe has to be adapted. When making colorants or any other paint we know just which pigment we will use in our recipe. Any other raw material requires an evaluation whether it suits the chosen pigment. A pigment is chosen from the point of view of price or colour shade which we can or want to get with a particular pigment.



**Figure 22:** Pigment deagglomeration [obtained by Elementis Specialties, Inc. products presentation].

As already mentioned pigments are defined as organic or inorganic materials. Their capability of colouring all kinds of materials (paper, ceramic, plastics) is the main reason for their use. Pigments are also used to improve corrosion protection and basic-acid resistance.

A pigment is the most important component of a colorant. The concentration of a pigment in a colorant should be as high as possible in order to bring in the base paint a higher concentration of a pigment. In case the concentration of a pigment is too high it will come to flocculation of a pigment. Level of pigmentation in colorants for inorganic pigments is 50 – 70 %, for organic pigments 15 – 35 %.



**Figure 23:** Primary particles, aggregates, and agglomerates according to DIN 53 206, part I [21].

When preparing paint or colorant we want to stabilise the pigment in primary particles (Figure 23). That is possible when a proper wetting and dispersing agent is in use (and normally also grinding is required).

Particles of different pigments have different shapes; some of them can be seen in Figure 23.

### **Pigments classification**

The most satisfactory way to classify a pigment is according to its source, because most of the significant properties which any pigment groups may have in common can be attributed to their composition. Different types of pigments are today available. In fact after the production of synthetic pigments various classes of pigments suited to different types of industries have evolved.

Inorganic Pigments are those that are made up of mineral compounds. Those minerals are mainly oxides and sulphides of one or more metals. Inorganic pigment can also be synthetic.

Inorganic pigments classification [22]:

1. White Pigments:
  - Titanium Dioxide
  - Zinc Sulfide Pigments
  - Zinc Oxide (Zinc White)
  
2. Coloured Pigments
  - Oxides and Hydroxides (**P.R.101**)
  - Cadmium Pigments
  - Bismuth Pigments
  - Chromate Pigments
  - Ultramarine Pigments
  - Iron Blue Pigments.

Many pigmented systems show typical colour or structural changes when subjected to intense radiation or weathering [23]. The best-known of these are yellowing, chalking, and loss of gloss [24]. These processes involve photochemical reactions in which the pigment can act as a catalyst or in which the pigment itself undergoes chemical changes [22].

Inorganic pigments are chemically very stable and are classes as one of the most stable colouring matters. This is especially true for oxide pigments which often have a highly protective effect on the substrate [25].

Resistance to light and weather generally depends on the chemical composition, structure, defects, particle shape and size, and concentration of the pigment [26]. However, these properties also depend on the medium in which the pigment is used.

## Organic pigments

Molecules in organic pigments are made of carbon atoms along with hydrogen, nitrogen and plant products.

Organic pigments list according to chemical constitution [27]:

### 1. Azo Pigments:

- Monoazo Yellow and Orange Pigments
- Disazo Pigments
- $\beta$ -Naphthol Pigments
- Naphthol AS Pigments (Naphthol Reds)
- Azo Pigment Lakes (Salt Type Pigments)
- Benzimidazolone Pigments
- Disazo Condensation Pigments
- Metal Complex Pigments
- Isoindolinone and Isoindoline Pigments

### 2. Polycyclic Pigments

- Phthalocyanine Pigments
- Quinacridone Pigments (**P.R.122**)
- Perylene and Perinone Pigments
- Diketopyrrolo Pyrrole (DPP) Pigments (P.O.73)
- Thioindigo Pigments
- Anthrapyrimidine Pigments (Anthraquinone Pigments)
- Flavanthrone Pigments (Anthraquinone Pigments)
- Pyranthrone Pigments (Anthraquinone Pigments)
- Anthanthrone Pigments (Anthraquinone Pigments)
- Dioxazine Pigments (**P.V.23**)
- Triarylcarbonium Pigments
- Quinophthalone Pigments

There are natural organic pigments and synthetic organic pigments. Natural pigments are derived from animals and plants but the use of these pigments is rare due to their poor light fastness stability. The synthetic organic pigments are carbon based and are often made of petroleum compounds.

Colorants are classified as either pigments or dyes. Pigments are inorganic or organic, coloured, white or black materials which are practically insoluble in the medium in which they are incorporated. Dyes, unlike pigments, do dissolve during their application and in the process lose their crystal or particular structure. It is thus by physical characteristics rather than by chemical composition that pigments are different from dyes [28]. In fact, both are frequently similar as far as the basic chemical composition goes, and one structural skeleton may function either as a dye or as a pigment [27].

### **Colour Index**

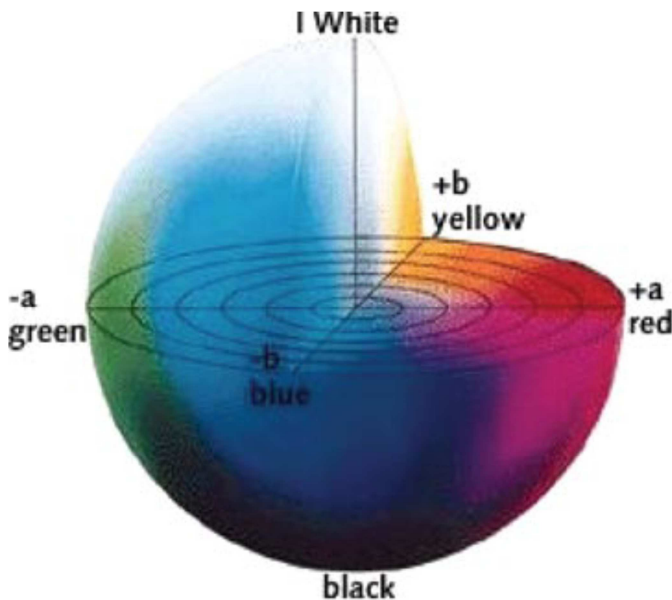
The **C.I. (Colour Index) Name** is an internationally recognized code assigned to a particular “colorant.” The C.I. Name consists of the category (type of dye or pigment), general hue and serial number assigned, based on its chemical composition. For example, P.B.60, Anthraquinone Blue, indicates a specific Pigment Blue. The C.I. Number is a five-digit reference number assigned in the Colour Index based on the chemical structure of a colorant, regardless of usage class [29].

### **Colour Space**

CIELab colour space is used to enable control over the different batches of pigments, pastes and colours and therefore offer quality of shades. In 1931 one of the first mathematically defined colour space CIE was created by the International Commission on illumination. Some changes were made in 1960 and 1976 (CIELab) but the main parameters stayed the same. The system from 1931 is limited because it does not uniformly express differences in lightness, purity and dominant wavelength between colours. Until now CIELab system has improved the organization of colours so that numeric differences between colours agree more consistently with the human visual perception.

Since CIELab defines colours more closely to the human colour perception, this system is often used in the quality control of coloured products. For example, once the colour of a production sample is located within the CIELab colour space, it is compared to the colour quality control production standard. The colour differences between the production sample and the standard are then determined and compared to predetermined acceptance tolerances.

The CIELab colour space (Figure 24) is based on the concept that colours can be considered as combinations of red and yellow, red and blue, green and yellow, and green and blue. To determine the exact combination of colours of a product, coordinates of a three dimensional colour space are assigned.



**Figure 24:** Sample of CIELab Colour Space [30].

The **L** coordinate of an object is the lightness intensity as measured on a scale from 0 to 100, where 0 represents black and 100 represents white.

The **a** coordinate of an object represents the position of the object's colour on a pure green and pure red scale, where **-a**(-128) represents pure green and **+a**(+127) represents pure red.

The **b** coordinate represents the position of the object's colour on a pure blue and pure yellow scale, where **-b**(-128) represents pure blue and **+b**(+127) represents pure yellow [29].

The centre of each axis is 0. A value of 0 or very low numbers of both **a** and **b** will describe a neutral or near neutral. In theory there are no maximum values of **a** and **b**, but in practice they are usually numbered from -128 to +127 (256 levels) [28, 29].

Interesting characteristic of the CIELab system is that the distance that can be calculated between colours, is directly proportional to the difference between the two colours as perceived by the human eye.



$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad [32]$$

**Equation 5:** Shows how hue difference between two colour shades is calculated.

Colour shades can look different at different light. In this work we only and always used the information at the D65 10Deg. That is outdoor daylight [33].

### **Pigment Volume Concentration (PVC) and Critical Pigment Volume Concentration (CPVC)**

In this thesis we use wetting and dispersing agents with high molecular (polymers) structure. The colorants were made with wetting and dispersing agents without any resin, which is normally used in coatings. Resin also improves stability of the pigment. Low-molecular wetting and dispersing agent would not provide the required stability of the pigment.

In this section it is also logical to explain that colorants can be prepared with a formulation where resin is included or not. Normally colorants with resin are prepared for the industrial coating. Since colorants prepared in this way are normally very expensive and handling with them has to be more precise this means higher costs of equipment because they are more exposed to the drying problem. This also means that the consumption of these colorants has to be in bigger volumes which are much more difficult to achieve with the colorants in decorative industry.

For the preparation of the colour shades in a certain product there is a known mathematical formula which helps to calculate the maximum concentration of the pigment which can be in use in the colour shades recipes in order to avoid quality problems. This formula is not directly prepared for colorants but for ready-to-use coatings.

Pigment volume concentration (PVC) is a key parameter of paints and coatings. Along with a few other parameters, PVC makes it possible to predict numerous interrelationships between a coating system's composition, and the resulting properties. PVC makes an equally effective tool for characterizing and classifying paints and coatings. ISO 4618 part 1 defines PVC as the ratio of pigment and filler volume in a coating film to the aggregate volume of non-volatile matter. This further implies that the binder is considered in its final, solid form, rather than as supplied [34, 35].

$$PVC = \frac{\Sigma V_{Pigments} + \Sigma V_{Fillers}}{\Sigma V_{Pigments} + \Sigma V_{Fillers} + \Sigma V_{Binders}} \cdot 100 = \frac{\Sigma V_{Pigments} + \Sigma V_{Fillers}}{\Sigma V_{Total}} \cdot 100$$

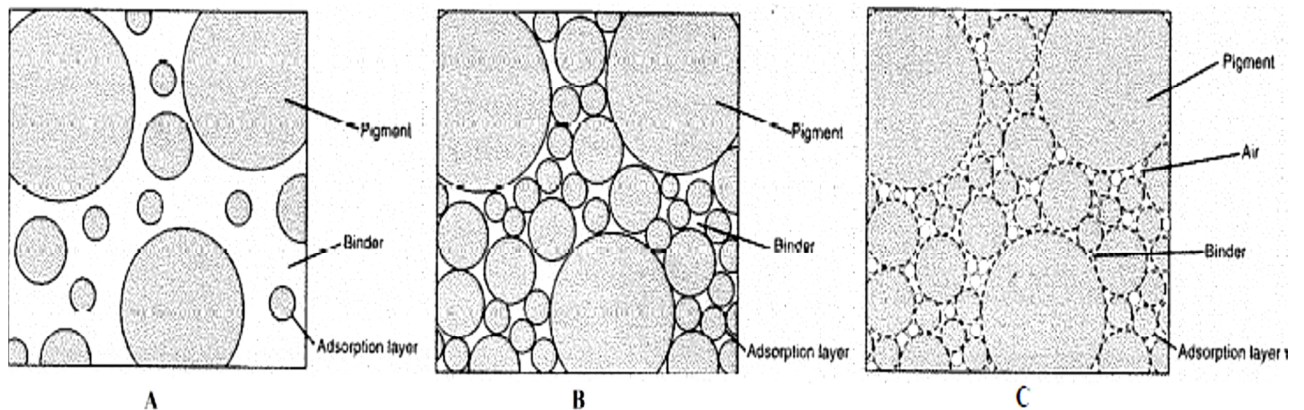
**Equation 6:** Definition of pigment volume concentration (PVC) [34].

ISO 4618 part 1 covers not just pigment volume concentration, but critical pigment volume concentration (CPVC) as well. CPVC is defined as the PVC at which binder just fills the voids between adjacent solid particles of pigment, filler, etc. in a coating film. Above this point, a number of properties experience significant change [34]. The methods of determining the CPVC are divided into two groups:

- 1) Methods based on the observation of a sudden change in properties in a series of PVCs (e.g., ion permeability, permeability to water evaporation, colour, gloss stability after coating with silk-luster paint).
- 2) Methods based on the experimental production of the dense pigment packing typical of CPVC, e.g., by means of oil absorption, filtration, vacuum filtration, or by measuring the volume of the supercritical film [22, 36].

$$CPVC [\%] = \frac{100\%}{1 + \frac{\rho_P}{\rho_B} \cdot \frac{OA}{100}}$$

**Equation 7:** Calculation of critical pigment volume concentration (CPVC) [34].



**Figure 25:** Schematic representation of conditions when A – PVC < CPVC; B – PVC = CPVC; C – PVC > CPVC [34].

Due to Equation 6 we could not calculate our PVC with dispersing and wetting agents. There is no known equation between the binder and the dispersing agent. The optimum volume of wetting and dispersing agents was found out by preparing

samples with different volumes of wetting and dispersing agents and sometimes also with different pigment volumes. By measuring their rheological and storage behaviours we could say which recipe has the best stability.

PVC is a calculation used for products with which a chemical engineer has to take into account that a certain volume of pigment will be added to them by colorants and this can mean that the CPVC is already reached. Because of this products prepared for being used with colorants have to be prepared in such a way that the PVC is never higher than the CPVC or better: engineers should calculate the limit which is not to be exceeded with the volume of colorants.

**Colorants in this work were prepared with the following pigments:**

VIOLET C.I.: P.V.23

MAGENTA C.I.: P.R.122

RED OXIDE C.I.: P.R.101

Hybrid orange pigment C.I.: (not defined)

Preparation of samples:

First we mixed the raw materials with a stick or with a mixer. If the sample was flowing than it was ready for the next stage - rubbing.

Rubbing was performed using a high speed dissolver produced by DISPERMAT (Figure 26). We were rubbing every sample for 40 minutes at the speed of 2500 circles per minute with the exception of the filler paste which was being rubbed for 20 minutes. Pearls were added to the sample. The container in which the sample was rubbed holds around 0.5 litre. We put in 200 ml of the sample and 200 ml of pearls. The dissolver also has a cooling system. The rubbing of the sample makes the temperature rise because of the shear stress which becomes stronger in the sample. By cooling the container we manage to keep the temperature below 30°C. Rubbing was needed for the deagglomeration of the pigment to the primary particle. Of course at first we did not know how much time was needed for rubbing our pigments and filler. With the first samples we checked the size of the pigment particles at different rubbing times. We found out that 20 minutes was the required time for the filler and 40 minutes for our four pigments to rub. The particles size in our samples had to be less than 20 µm. The size of particles in the samples was measured with a

grind meter. The rubbing machine in Figure 26 can be used also for other paint products. As can be seen from the picture, the machine has a motor which can work at different speeds. Apart from speed we can also regulate its height.



**Figure 26:** Rubbing machine for the paint pastes [37].

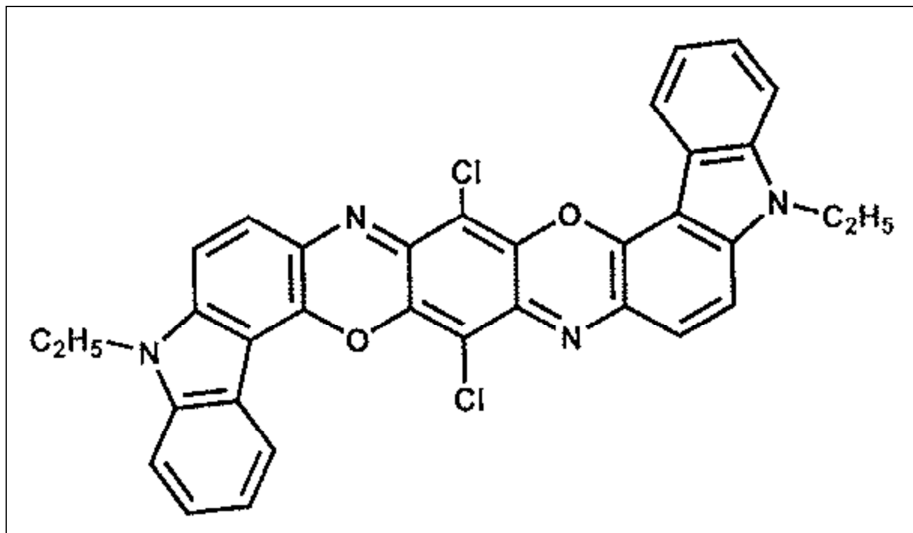
After rubbing we normally add deaerators to the samples since rubbing causes the formation of a lot of foam.

### ***3.8.2.1. Organic violet pigment (C.I.: P.V.23)***

The carbazole pigment (C.I. Pigment Violet 23) is the most important and commercially used form of dioxazine derivatives [38]. Its violet colour has a blue-redden hue that cannot be reproduced with a mixture of pigments. The crystallographic analyses have shown an angular structure of the molecule (Figure 27) [39].

Because of its high chemical resistance that is similar to the phthalocyanine blues, the C.I. Pigment Violet 23 is frequently used in tinting paints. It can also be used to mask the yellowish aspect in white solvent coatings. To full fill this role, the pigment must be well dispersed.

Synonym for the pigment is 8,18-Dichloro-5,15-diethyl-5,15-dihydrodiindolo(3,2-b:3',2'-m)tri-phenodioxazine [40].



**Figure 27:** Molecular structure of the C.I. Pigment Violet 23 [28].

Unfortunately, it is difficult to prepare a stable and fine dispersion of the C.I. Pigment Violet 23 by means of grinding in an organic medium. Additives are always used to solve problems related to bad pigment dispersion, viscosity increase on storage and thixotropy. Indeed, the experience shows that C.I. Pigment Violet 23 concentrates have high tendency to gel on storage if an adequate dispersant is not used or when its dose is not optimized. The consequences is usually a low tinting strength that requires consumption of larger amounts for tinting. On the other hand, the increase in viscosity causes big troubles in automatic tinting [41].

Typical properties of the pigment which we used:

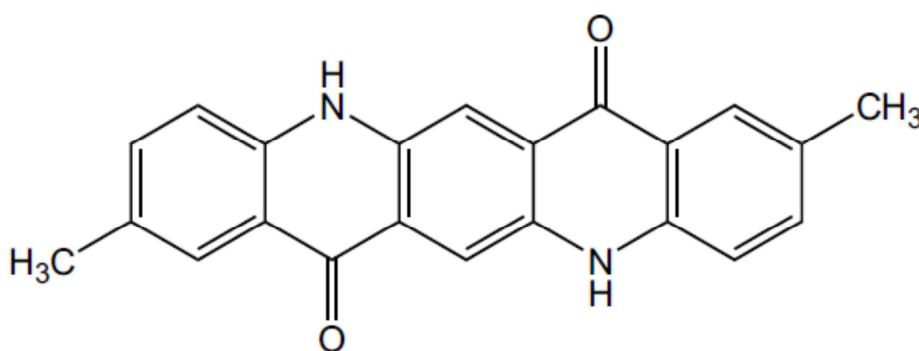
- Specific gravity 1.5 g/cm<sup>3</sup>
- Oil absorption 49 g/100g
- Acid resistance 5.0
- Alkali resistance 5.0

Alkali and acid resistance are two pieces of information provided by pigment producers and given with scale from 1 to 5, where 1 means bad resistance and 5 a very good resistance.

### 3.8.2.2. Organic magenta pigment (C.I.: P.R.122)

For our work we used one of commercially available quinacridone pigments. It possesses excellent fastness to migration and outstanding heat stability. P.R. 122 offers a very clean bluish shade of red, which is usually referred to as pink or magenta [28].

Synonym for the pigment is 5,12-Dihydro-2,9-dimethylquino[2,3-b]acridine-7,14-dione [42].



**Figure 28:** Molecular structure of the C.I. Pigment red 122 [43].

Organic magenta pigment red 122 is one of the most expensive pigments.

Taking P.R. 122 pigment to prepare a colorant is quite a difficult task since this colorant is rarely used in colour formulations. This means that the colorant will stay in a canister longer than the others and should therefore show a stable formation. For violet as well as for magenta colorants it is known that viscosity increases on storage. Moreover, thixotropy can increase too.

Typical properties of pigment which we used [44]:

- Specific gravity 1.4 g/cm<sup>3</sup>
- Oil absorption 59 g/100g
- Acid resistance 5.0
- Alkali resistance 5.0

### 3.8.2.3. Inorganic red oxide pigment (C.I.: P.R.101)

The continually increasing importance of iron oxide pigments is based on their non-toxicity, chemical stability, wide variety of colours ranging from yellow, orange, red,

brown, to black; and low price [23]. Pigment P.R.101 which we use is a synthetic inorganic pigment chemical red iron oxide.

$\text{Fe}_2\text{O}_3$  – iron (III) oxide

Typical properties of pigment which we used [45]:

- Specific gravity 5.0 g/cm<sup>3</sup>
- Oil absorption 18 g/100g
- Acid resistance 5.0
- Alkali resistance 5.0

#### ***3.8.2.4. Hybrid orange pigment***

In our recipe we use P.O.73 which is organic. It is made by a proprietary co-finishing process to attach the organic high performance pigments to the surface of the inorganic titanium yellows to improve cleanliness, opacity, and gloss when compared to traditional physically blended products. This pigment also provides outstanding durability in comparison to typical formulations using titanium dioxide in conjunction with high performance organic pigments. With their excellent dispersion properties and low dusting characteristics it is comparable to an inorganic pigment and that is why it is called Hybrid orange pigment [46]. This pigment was taken due to the exterior stability which is improved in this orange pigment. Typical properties of the pigment which we used [47]:

- Specific gravity 2.5 g/cm<sup>3</sup>
- Oil absorption 26 g/100g
- Acid resistance 5.0
- Alkali resistance 5.0

#### **3.8.3. Solvents, filler, defoamers and deaerators**

##### **Solvents**

Solvents in colorants can be solventborne, solventborne with VOC free or waterborne. Which solvent is used depends on the products for which the prepared colorants will be used. The right choice of solvents effects on storage stability of the colorants and rheological properties.

Coatings normally contain solvents which evaporate during the application and film formation. Usually solvents are in the liquid form and they are capable of dissolving other substances (solid, liquid or gas) and changing them into the liquid form without their chemical change. In coatings solvents are used to dissolve resin and therefore effect the reduction of viscosity. Solvents do not only affect spilling and flowing, but also the appearance, physical properties and fastening of the coating [48, 49].

### **Fillers**

We use fillers to make the recipe cheaper and they also help us improve the rheological behaviour of paint or colorant. At the same time fillers have no opacity and no colouristic effect which makes them very useful in paint or colorant recipes since they can be used for colour strength regulation.

Given the diversity of mineral fillers, it is helpful to divide them into various categories. Categories like carbonates, silicates, silicas (silicon dioxides), sulphates, oxides and organic fillers include well know as well as more obscure materials. In addition to this type of categorisation, fillers are also grouped according to their natural versus synthetic origin [35].

### **Defoamers and deaerators**

Foam is one of the most common problems which a formulator has to consider when developing coatings, paints, and print inks. It is particularly important in waterborne, radiation-curing, solvent-free or high solids formations. The problem of foam is usually easy to recognize, since foam bubbles form in a container after filling. Foam is also clearly visible when applying paint to a substrate by brush or by roller. There are however numerous other problems where the connection with foam is not immediately obvious [50, 51]. For example pinholes and clouding loss of gloss.

If the substrate for industrial coating shows early signs of corrosion the cause may be pinholes in the paint. Pinholes are small channels in the coating which remain when foam bubbles rise too slowly out of the drying paint layer. If these channels reach down to the metallic substrate, moisture and salts can penetrate unhindered resulting in progressive corrosion [50].

If a coating does not develop gloss or becomes cloudy immediately after application, the initial response is to suspect incompatibility of the components of the paint.



However inspection using a microscope or even a simple magnifying glass reveals that cloudiness or low gloss is sometimes caused by extremely fine air bubbles trapped in the dry paint film [50].

Luckily we have defoamers and deaerators which help us avoid foam in our systems. Foam is a stable distribution of small gas bubbles (usually air bubbles) in a liquid system. Pure liquids do not foam. Only if surfactants are present in the liquid can stable foam occur.

Current terminology distinguishes between defoamers and deaerators. In waterborne formulations, defoamers destroy the macro-foam on the surface and prevent large air entrapments. Deaerators evacuate the finely dispersed air out of the paint film as quickly as possible during application. In practice differentiation is not usually so clear cut. Thus defoamers are also effective to some extent against micro-foam. Both additives are active at the surfactant-stabilized air/liquid interface [52].

### **3.8.3.1. Solvents**

The decision to use VOC-free solvents and water was easy because in the future the decorative paint industry will have more VOC-free products. The combination of water and glycol solvents is necessary in order to slow down evaporation of the solvents out of the system. With the use of glycol we also predicted better compatibilities of the universal colorants with solventborne products (bases) [53].

We used glycerol – otherwise identified as 1,2,3-propanetriol. The boiling point of the glycerol we used is 290°C which means that it is VOC-free.

Typical properties:

- Physical state is liquid
- Colourless to light yellow
- pH 5 to 8
- Density approximately 1.29 g/cm<sup>3</sup> at 25°C
- Solubility completely with water and ethanol

Maximum storage period is 12 months.

### 3.8.3.2. Fillers

We tested only two fillers: MICROTALC and FINNTALC. The difference between the two of them is presented by the following data obtained from a producer.

<b>MICROTALC</b>	/	<b>FINNTALC</b>
<b>Mineralogy:</b>		
Talc (Mg – Silicate) present 95 %.	/	96 %
Residue is from chlorite and quartz.	/	Residue magnesite and chlorite
 <b>Chemical analysis of the Microtalc:</b>		
MgO - 32 %,	/	31 %
SiO <sub>2</sub> - 60 %,	/	60 %
Al <sub>2</sub> O <sub>3</sub> – 0.1 %,	/	0.5 %
FeO total – 0.1 %,	/	2.2 %
Insoluble in HCl(1:3) 95%(ISO 3262-2),	/	Fe acid soluble 0.2%(1mol/L HCl,100°C)
Loss on ignition 7.0 % (DIN 51081/1000°C),	/	5.8 %
Water soluble 0.2 % (ISO 787/3),		
pH value 9.5 (ISO 787/9).	/	9.1
 <b>Optical properties:</b>		
Brightness R <sub>y</sub> 96 % (DIN 53163),	/	84 %
CIE L*, a*, b* 98.5/0/1,1 (DIN 6174),	/	93.5/-0.3/1.6
Yellowness index 2 (DIN 6167).	/	2.4
 <b>Physical properties:</b>		
Median particle size 1.7 µm (d50 %)	/	4.5 µm
Specific surface area 9.2 m <sup>2</sup> /g (BET, ISO 4652),	/	6.0 m <sup>2</sup> /g

The main difference between these two fillers which can affect colorants and paint properties lies in their particle size.

We decided to use finntalc since no difference from microtalc was noticed in its effect. In some cases, when the volume of filler in the recipe is bigger than the

particle size of the filler, this can affect the haze and gloss of the material. If particles of the filler are bigger, then the gloss is lower and the haze is bigger.

### **3.8.3.3. Defoamers and deaerators**

Foam can occur by stirring and rubbing colorants during manufacture. We tested three defoamers and one deaerator. The defoamers were used in the grinding and the deaerator in the let-down stage.

Technical data in the section below are from the producer of those raw materials.

#### **Defoamer 1**

Defoamer 1 is recommended for aqueous coatings based on polyurethane dispersions and polyurethane/acrylic combinations. It is also effective for defoaming pigment concentrate formulations.

Typical properties:

- Density at 20°C in is 0.90 g/ml
- Non-volatile matter is 60 %, solvents: Di-propylene glycol monomethyl ether
- Recommended levels 0.1 to 1.0 % additive (as supplied) based upon total formulation
- Due to the high activity, this additive should be incorporated under high shear in order to achieve optimal distribution of the defoamer. Otherwise, defects in the system can occur

Composition of defoamer 1 is a solution of polydimethylsiloxane (PDMS) modified polyether. Storage stability is 24 months in unopened containers.

#### **Defoamer 2**

Defoamer 2 is recommended for waterborne formulations. It is excellent for binder-free and binder containing pigment concentrates. It is highly compatible and the risk of surface defects is minimized.

Typical properties:

- Appearance is slightly hazy liquid
- Active matter content 100 %

- Recommended levels are 0.5 to 2.5 % for pigments concentrates as supplied, calculated on total formulation
- Addition may be either in the grind or during the let-down procedure

The chemical description of defoamer 2 is: organic polymer, silicone-free, contains fumed. Storage stability is 12 months in unopened containers.

### **Defoamer 3**

Defoamer 3 is an emulsion with an excellent stability and defoaming persistency. The defoamer 3 is miscible with water in all ratios.

Typical properties:

- Appearance is liquid
- Active matter approximately 25 %
- Density at 20°C approximately 1.01 g/cm<sup>3</sup>
- Recommended levels are 0.1 to 1.0 % on total formulation
- Addition may be either in the grind or during the let-down procedure

The composition of defoamer 3 is an emulsion of modified fatty, hydrophobic silica, alkoxyated compounds, polysiloxane copolymer and emulsifiers.

The minimum shelf life in closed containers is 6 months from the date of dispatch.

### **Deaerator 1**

Deaerator 1 is recommended for waterborne formulations and can be used universally in clear and pigmented formulations.

Typical properties:

- Appearance is liquid
- Active matter content 100 %
- Recommended levels are 0.1 to 1.5 % depends in which coating it is used
- Additive should be incorporated under high shear

Chemical description of deaerator 1 is: polyether siloxane copolymer, contains fumed silica.

Storage stability is 12 months in unopened containers.

## **4. Experimental results**

Before introducing the recipes of the colorants we should first discuss the filler paste a bit more in detail. At the beginning (as can be seen from the tables below) the filler was added as a raw material. During the tests we noticed that it would be better to have filler prepared in the form of a semi-manufactured good. This was the key also for the corrections required in the production plant. So the filler paste is prepared just like a colorant where in some recipes instead of the filler or another raw material the filler paste is used.

### **4.1. Rheology measurements**

While we were using different raw materials and in different values rheology measurements were the main methods providing the essential directions.

Our first goal was the preparation of colorants with stable rheological parameters. After that we continued with other tests: on other properties of the colorants (compatibility, wetting test, dispensing,..). Of course the tests of the behaviour of the colorants on some of the versions were parallel to rheological tests.

#### **4.1.1. Filler paste**

A filler paste is a useful semi-manufactured product because it enables simple and fast corrections in the production plant. In Table 5 and 6 it can be seen how we were changing the recipes in order to get a satisfactory result. At the beginning we were looking for a way to obtain viscosity of the filler paste which would not affect rheological parameters of colorants when the filler paste would be added. After that our next objective was to have a stable filler paste for at least three weeks which was monitored with a stove at temperature 40°C.

**Table 5:** Recipes of filler paste from V-1a to V-6.

Version of filler paste:	V-1A [g]	V-1B [g]	V-2 [g]	V-3 [g]	V-4 [g]	V-5 [g]	V-6 [g]
Water	31.25	31.25	39.00	43.70	42.20	41.00	40.00
Glycerol	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Defoamer 1	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Wetting and dispersing agent 1	8.50	8.50	8.70	4.00	0.50		3.00
Dispersing agent 2		1.00			1.00	2.50	
FINNTALC						50.00	50.00
MICROTALC	43.95	43.95	46.00	46.00	50.00		
Rubbing 20 minutes							
Deaerator 1	0.30	0.41	0.30	0.30	0.30	0.30	0.30
<b>Σ</b>	90.00	91.11	100.00	100.00	100.00	99.80	99.30

Wetting and dispersing agent 1 is one of products with two functions. One is to wet the pigment and another to improve the dispersing of the pigment. Both are essential in colorant formulations. It can be used for inorganic and organic pigments; their characteristics are normally workable in both systems.

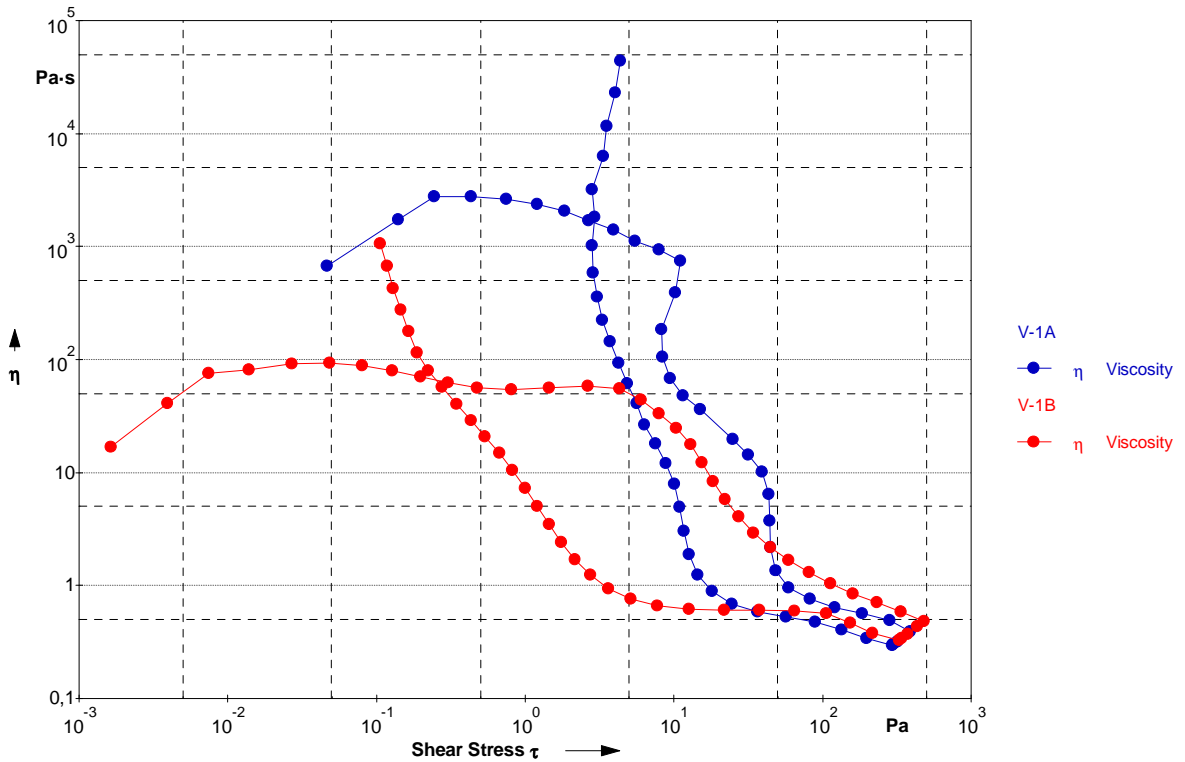
Dispersing agent 2 is a product which renders a better dispersing of the pigment. This product gives a better dispersing only when it is used in combination with inorganic pigments (from technical data sheet of the raw material).

**Table 6:** Recipes of filler paste from V-6A to version P1.

Version of filler paste:	V-6A [g]	V-7 [g]	V-7A [g]	V-8 [g]	Version P1 [g]
Water	36.0	34.0	34.0	34.0	34.7
Glycerol	5.0	2.0	2.0	2.0	2.0
Defoamer 1	1.0	1.0	1.0	1.0	1.0
Wetting and dispersing agent 1	2.0	2.7	2.7	2.5	2.5
Dispersing agent 2			0.7	1.5	1.5
FINNTALC	55.0	60.0	60.0	58.0	58.0
MICROTALC					
Rubbing 20 minutes					
Deaerator 1	0.3	0.3	0.3	0.3	0.3
<b>Σ</b>	99.3	100.0	100.7	99.3	100.0

Recipes in some cases - like V-1A and V-1B - have numbers which are changed for 0.01. This change is a result of the addition of certain raw materials during the rubbing phase. After the first recipe had not shown the required results (rubbing was not achieved, too low or too high viscosity of the rubbing material), we added raw materials during the rubbing phase.

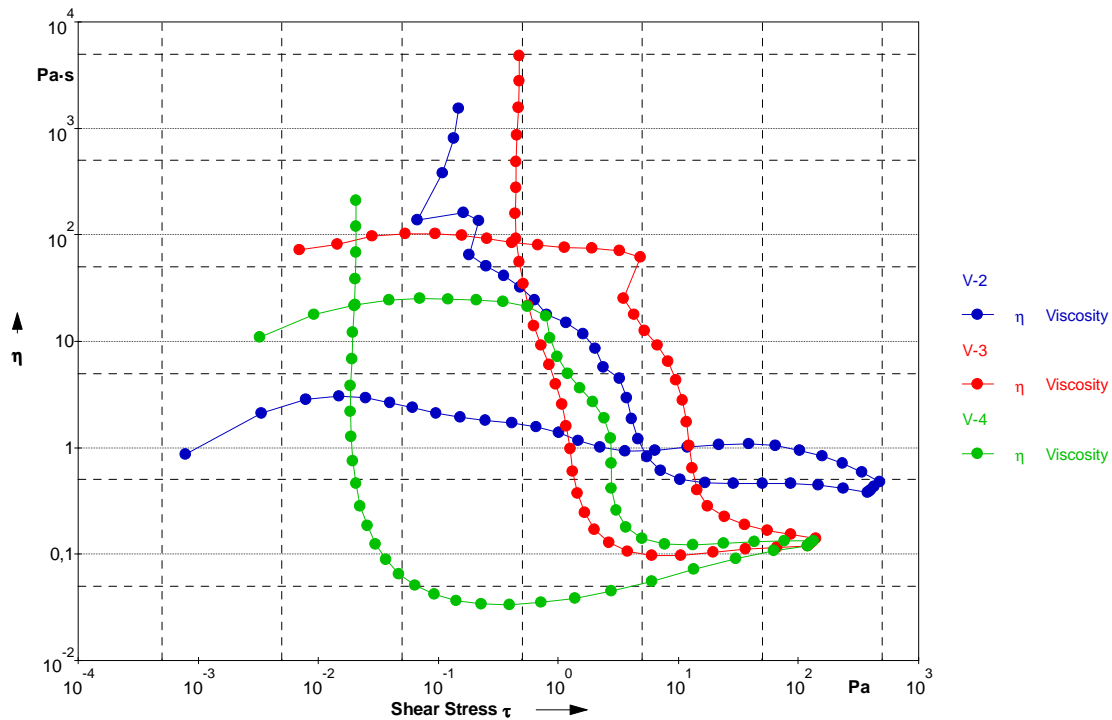
**Rheology results for the filler paste.**



**Graph 1:** Flow curves of the following filler pastes (for the samples): V-1a and V-1b.

V-1a – We take 8.5 % of wetting and dispersing agent as suggested from the wetting and dispersing agent producer for that quantity of filler. From Graph 1: too low viscosity at shear stress  $10^{2.5}$ Pa.

V-1b – We add 1% of dispersing agent 2. Graph 1 indicates a progress; the structure is not so strong at low shear stress and there is also an improvement of viscosity at high shear stress.



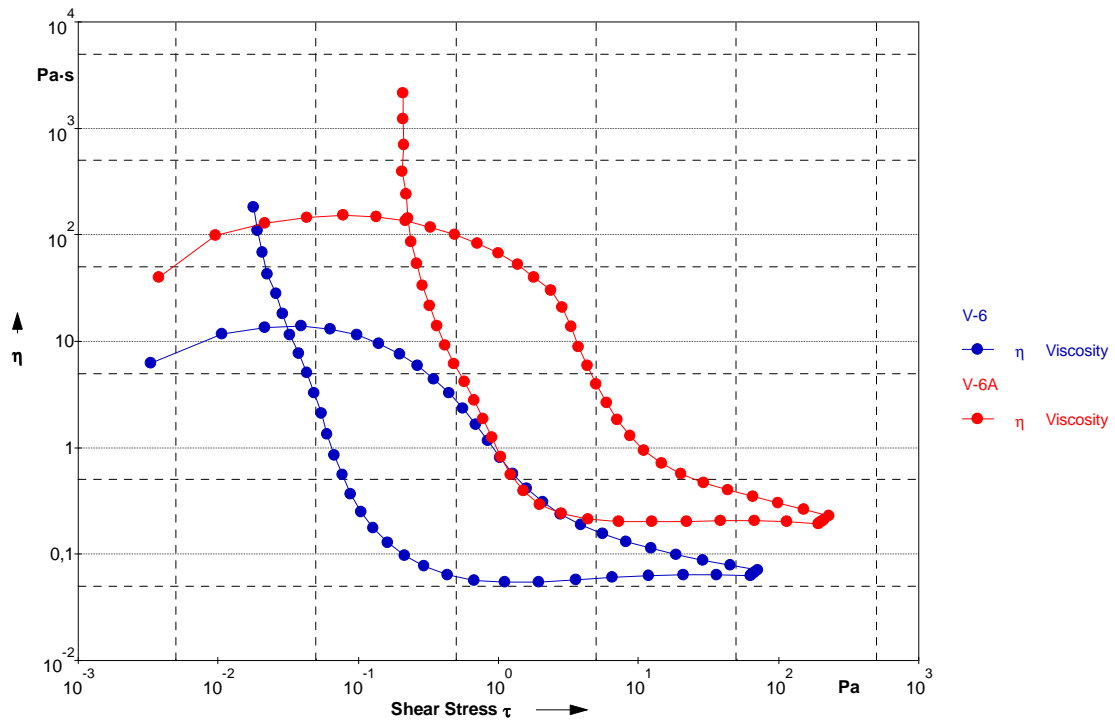
**Graph 2:** Flow curves of the following filler pastes (for the samples): V-2, V-3 and V-4.

V-2 – We increase Microtalc-filler, water, wetting and dispersing agent 1. We take out dispersing agent 2. Viscosity at high shear stress has improved but the structure of the sample is too low: filler could sediment (Graph 2).

V-3 – We increase water to get milling paste with low viscosity in order to avoid problems in the production plant. Simultaneously we decrease wetting and dispersing agent 1 to lower the costs. As can be seen from Graph 2 this has not provided good results. Structure of the sample is too strong and the milling paste still has high viscosity; this can result in problems in the production plant. Viscosity is still low.

V-4 – We add 1% of dispersing agent 2 and decrease wetting and dispersing agent 1. Graph 2 shows dilatant flow behaviour, which means that the level of wetting and dispersing agent is low. At this point we decide to go with different filler (finntalc).



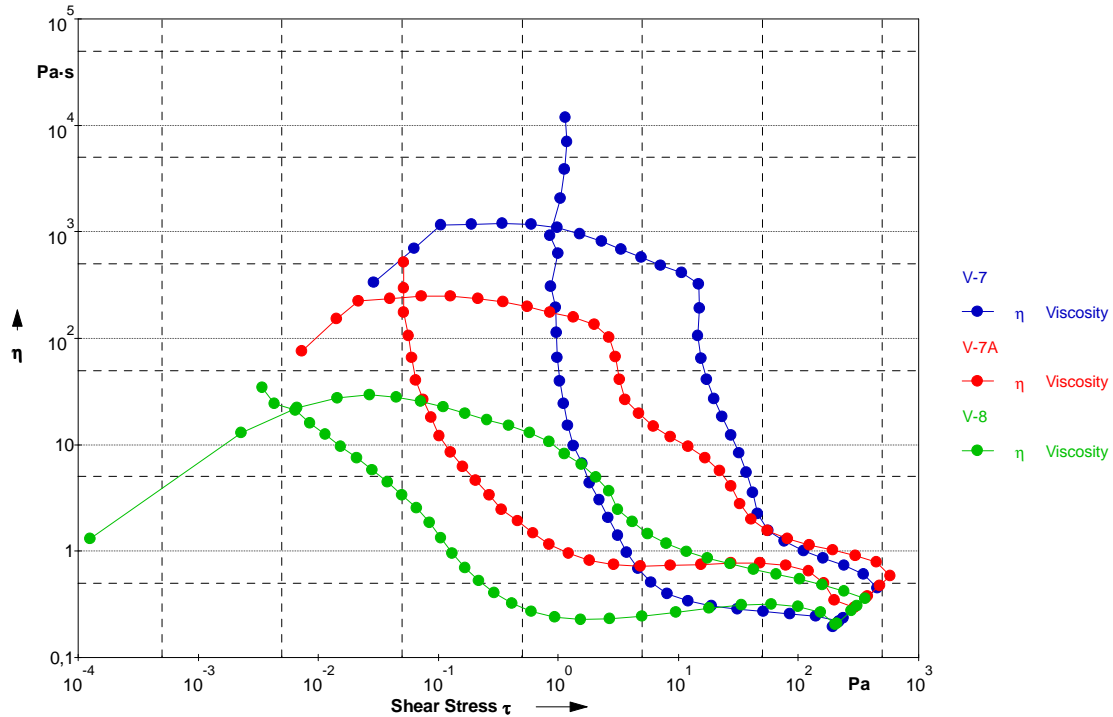


**Graph 3:** Flow curves of the following filler pastes (for the samples): V-6 and V-6A.

V-5 – We do not do the rheology measurement, because the result is predictable. The sample is too tough and wetting and dispersing agent 2 is missing. This is the first version with finntalc (Table 5).

V-6 – We add wetting and dispersing agent 2 and doing this makes the flow curve look good; the only problem is that it is too low (Graph 3).

V-6a – We add more finntalc and decrease the amount of water (as can be seen from the Graph) and the flow curve moves up (Graph 3).

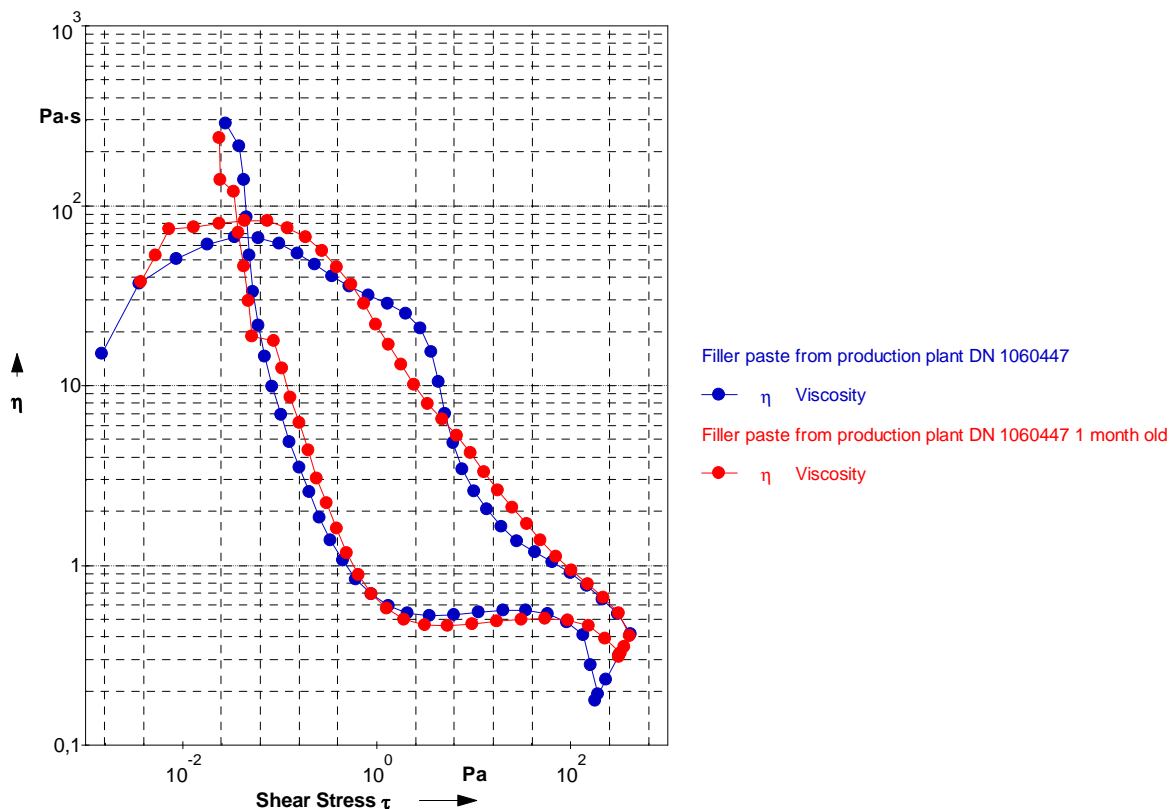


**Graph 4:** Flow curves of the following filler pastes (for the samples): V-7, V-7A and V-8.

V-7 – We increase finntalc, wetting and dispersing agent 1. We also decrease water in order to get a more viscous sample at high shear stress. Viscosity rises but also does pseudoplasticity (Graph 4).

V-7a – We add dispersing agent 2 and we get a less pseudoplastic sample. Moreover the milling paste becomes less viscous. That should also help to an easier production of the product in the production plant (Graph 4).

V-8 – To avoid problems in the production plant we even increase dispersing agent 2 (Graph 4).



**Graph 5:** Flow curves of filler paste (for the samples) version 2 and the red curve represents the same sample being in the stove for more than a month.

Version P1 – we go to the production plant with the recipe of the V-8 sample with 0.7 % more water. The result is expected and confirms stable rheology properties also after having aged the sample in the stove at 40°C for one month.

#### 4.1.2. Violet C.I.:P.V.23

Violet colorant is the first colorant we produced and as can be seen with the first versions V-1 to V-3 we were trying to produce the colorant without a filler paste. Our goal in the first versions is to prepare a stable colorant with filler. After making some versions we decide to first prepare a filler paste which will help us in the current recipes as well as when the colorant will have to be optimized in the production plan.

**Table 7:** Recipes of violet colorant from sample V1 to V5.

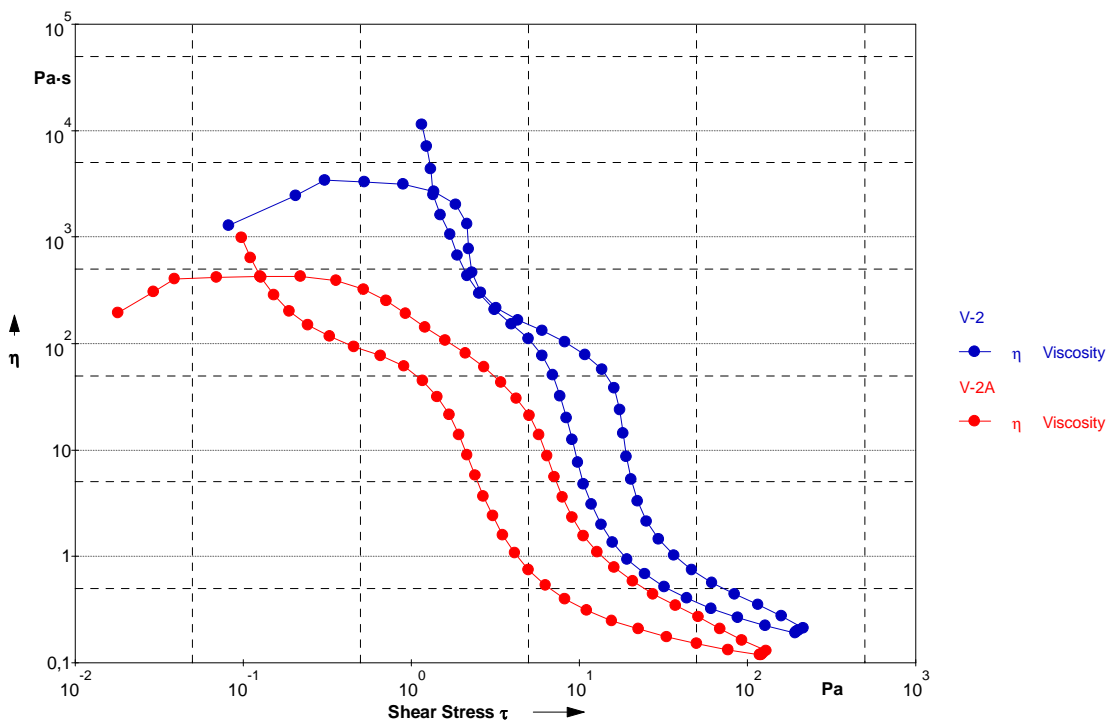
Version:	V-1 [g]	V-1a [g]	V-2 [g]	V-2a [g]	V-2b [g]	V-2c [g]	V-3 [g]	V-4 [g]	V-5 [g]
Water	56.0	47.6	30.0	30.0	30.0	30.0	36.0	14.5	10.0
Glycerol	5.0	4.3	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Defoamer 1	1.0	0.9	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Wetting and dispersing agent 1	2.5	2.1	11.0	11.0	11.0	11.0	12.0	2.0	2.0
MICROTALC	37.5	31.9	28.0	28.0	28.0	28.0	30.0		
Filler past version V-8									34.0
Pigment: Violet P.V.23	10.0	8.5	10.0	10.0	10.0	10.0	10.0	8.0	8.0
Rubbing 40 minutes									
Filler past version V-8								34.0	34.5
Water				5.0	10.0	15.0	6.1	35.0	5.0
Deaerator 1		0.4	0.3	0.3	0.3	0.3	0.3	0.5	0.5
<b>Σ</b>	112.0	95.7	85.3	90.3	95.3	100.3	100.4	100.0	100.0

We started the tests with versions V-1 and V1-A by applying low values of wetting and dispersing agent 1 which is also recommended by the producer. The problem was that those two samples had sediments. In order to prevent the sedimentation we increased the wetting and dispersing agent 1.

**Table 8:** Recipes of violet colorant from sample V6 to V8D.

Version:	V-6 [g]	V-6c [g]	V-6b [g]	V-7a [g]	V-7b [g]	V-8 [g]	V-8a [g]	V-8b [g]	V-8c [g]	V-8d [g]
Water	5,0	10,0	10,0	5,0	8,0	3,0	3,0	3,0	3,0	3,0
Glycerol	5,0	5,0	5,0	5,0	2,0	3,0	3,0	3,0	3,0	3,0
Defoamer 1	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0
Wetting and dispersing agent 1	6,0	6,0	6,0	6,0	6,0	6,0	6,0	6,0	6,0	6,0
MICROTALC										
Filler past version V-8				70,0	70,0	70,0	70,0	70,0	70,0	70,0
Pigment: Violet P.V.23	8,0	8,0	8,0	8,0	8,0	8,0	8,0	8,0	8,0	8,0
Rubbing 40 minutes										
Filler past version V-8	70,0	69,5	65,0			4,3		6,8	3,3	
Water	4,5		4,5	4,5	4,5	4,5	2,0	2,0	5,5	8,8
Deaerator 1	0,5	0,5	0,5	0,5	0,5	0,2	0,2	0,2	0,2	0,2
<b>Σ</b>	100,0	100,0	100,0	100,0	100,0	100,0	93,2	100,0	100,0	100,0

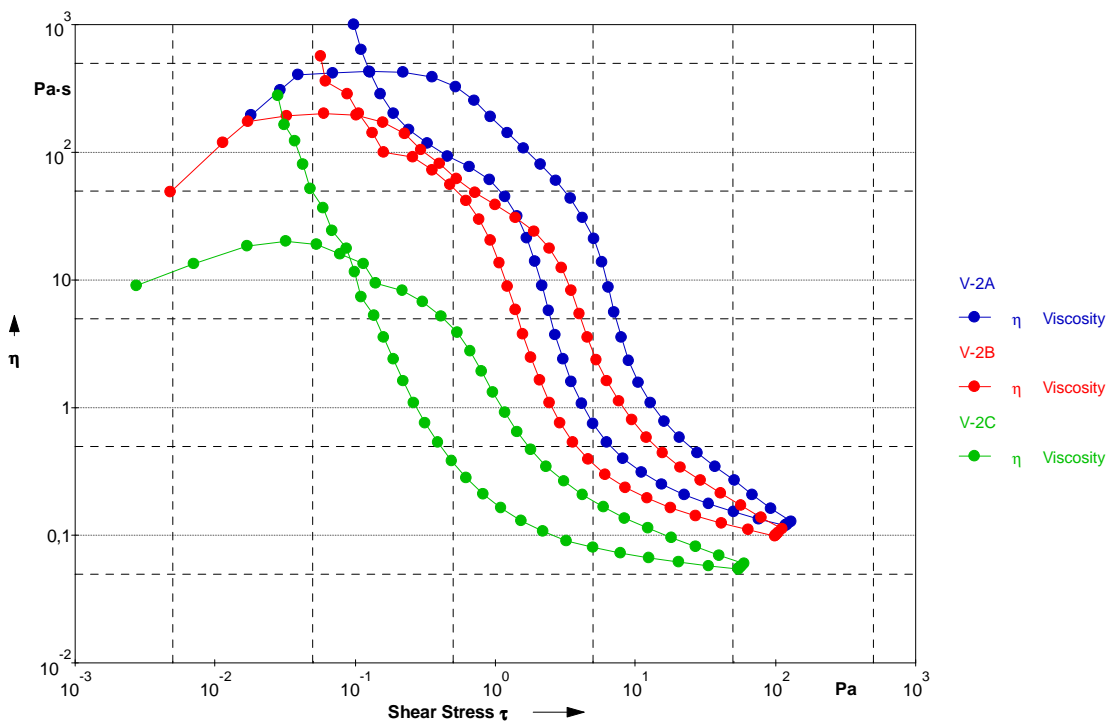
**Rheology results for the violet colorant, flow curves.**



**Graph 6:** Flow curves of the violet colorant V-2 and V-2A samples.

V-2 – We increase wetting and dispersing agent 1. The structure of the sample is stable. Sedimentation does not appear (Graph 6).

V-2A – In this sample we increase the amount of water to get information about how the colorant will behave. As expected viscosity at high shear stress drops for a little less than 0.1 Pas (Graph 6).



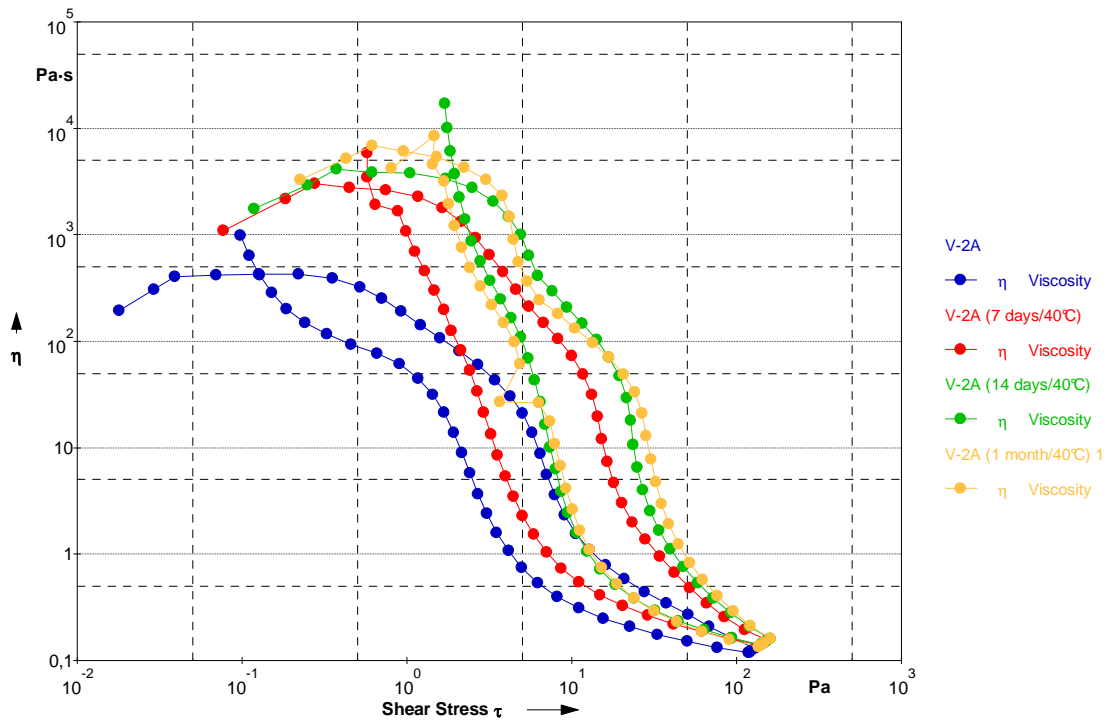
**Graph 7:** Flow curves of the following samples: violet colorant V-2A, V-2B and V-2C.

V-2A – We increase water for 5% due to V-2.

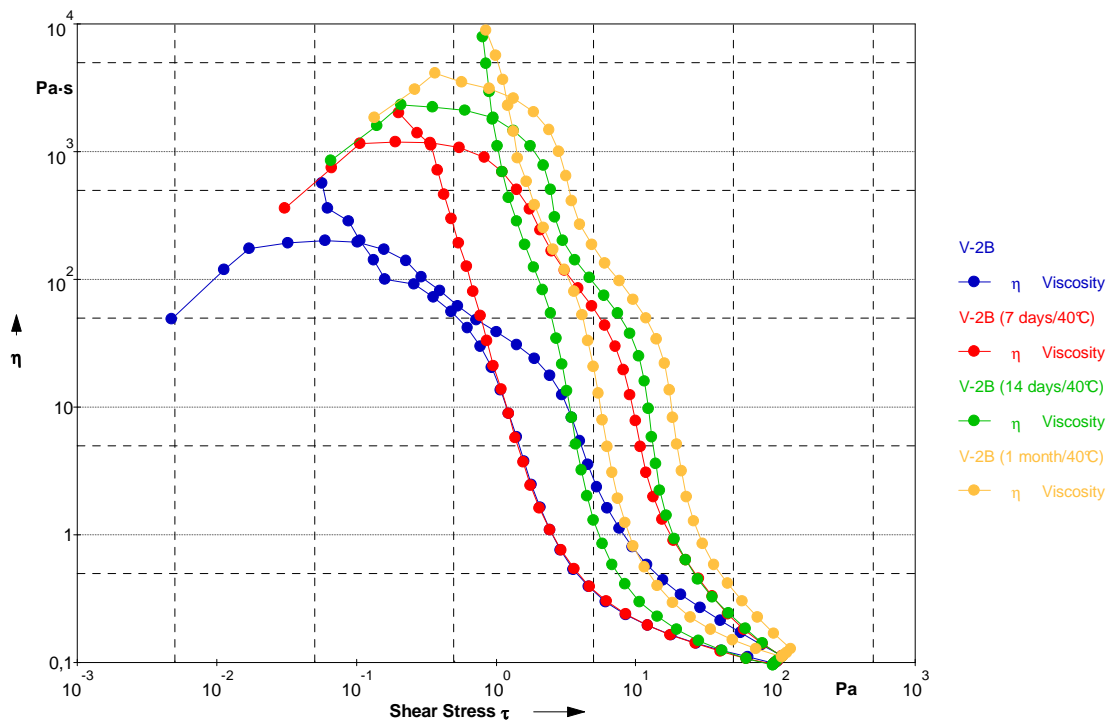
V-2B – We increase water for 5% due to V-2A.

V-2C – We increase water for 5% due to V-2B.

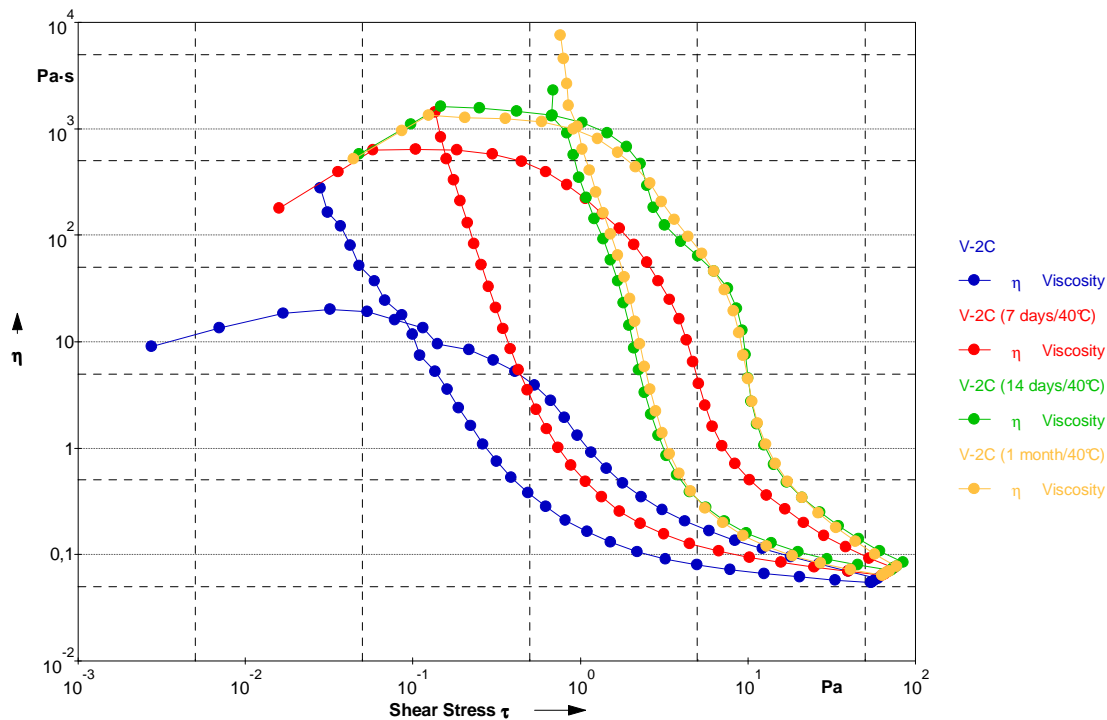
Graph 7 shows flow curves indicating the change of viscosity when water is added.



**Graph 8:** Flow curves of the following samples: violet colorant V-2A, V-2A (7days/40°C), V-2A (14days/40°C) and V-2A (1month/40°C).



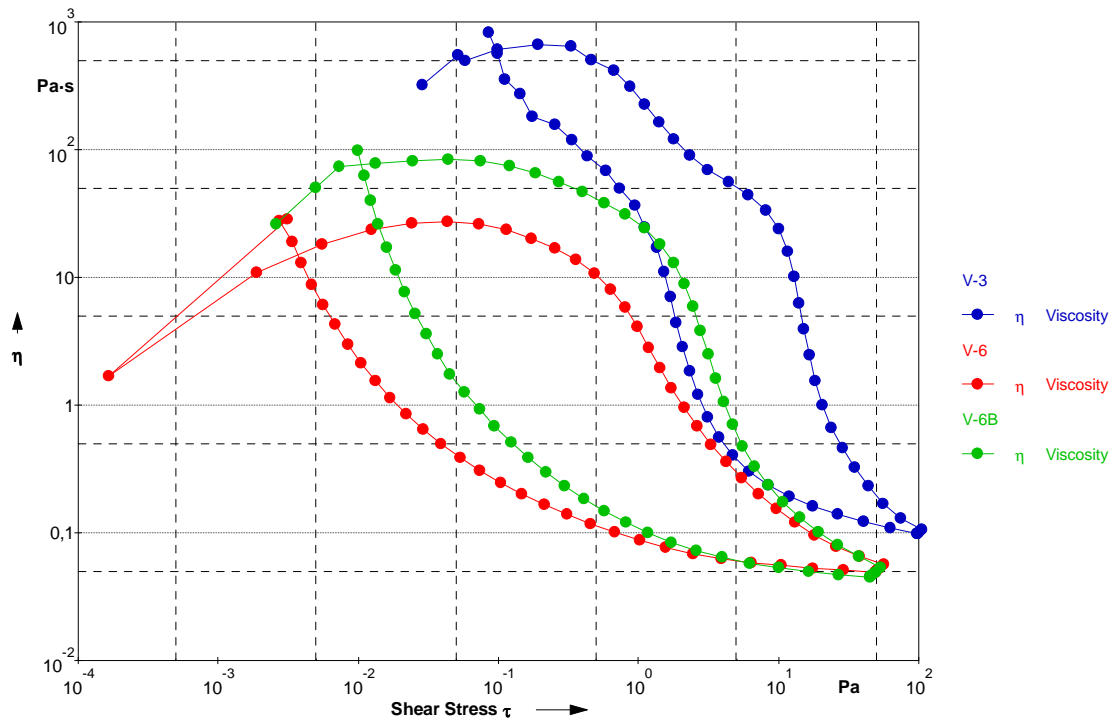
**Graph 9:** Flow curves of the following samples: violet colorant V-2B, V-2B (7days/40°C), V-2B (14days/40°C) and V-2B (1month/40°C).



**Graph 10:** Flow curves of the following samples: violet colorant V-2C, V-2C (7days/40°C), V-2C (14days/40°C) and V-2C (1month/40°C).

Graph 8, Graph 9 and Graph 10 show rheological changes on the samples during storage in a stove for 1 month at 40°C. The flow curves show how the samples were becoming more and more pseudoplastic; this is evident because viscosity at low shear stress was higher with every period. There was very little water evaporation which can be explained on the Graph by the rising of the flow curves at high shear stress. The difference among those samples in their rheological behaviour was in viscosity at low shear stress: the V-2C sample showed a significant difference in flow curves than the V-2A and V-2B samples. We can say that out of those three samples V-2B was the most stable due to its viscosity at low shear stress. However all the three were more or less on the same stability range since their viscosity at high shear stress hardly changed at all.



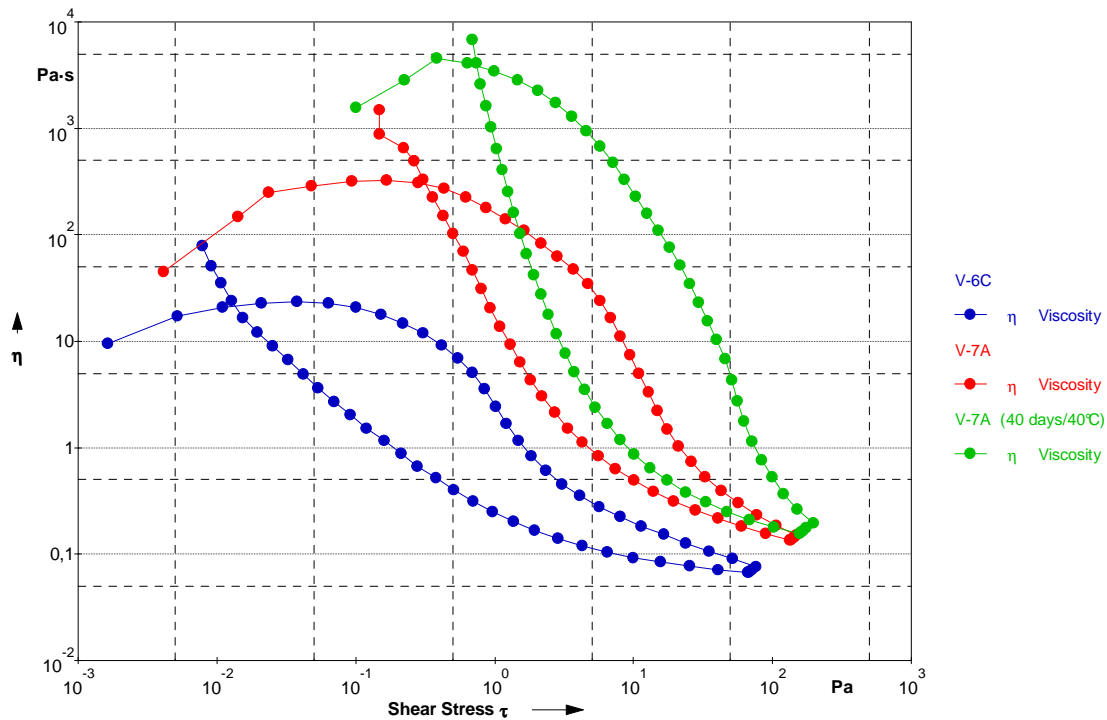


**Graph 11:** Flow curves of the following samples: violet colorant V-3, V-6 and V-6B.

V-3 – We add water due to the results from the V2 – V2C samples and we add wetting and dispersing agent. The result was not what we wanted: flow curve V-3 still shows strong pseudoplastic stability (Graph 11).

This is the last sample with microtalc-filler. All the subsequent samples have their filler pastes made of finntalc-filler. Versions V-4 and V-5 are not good enough for testing with rheometer – it would be pointless. Both show sedimentation and too high viscosity at low shear rate (that is evident when stirring the samples with a stick).

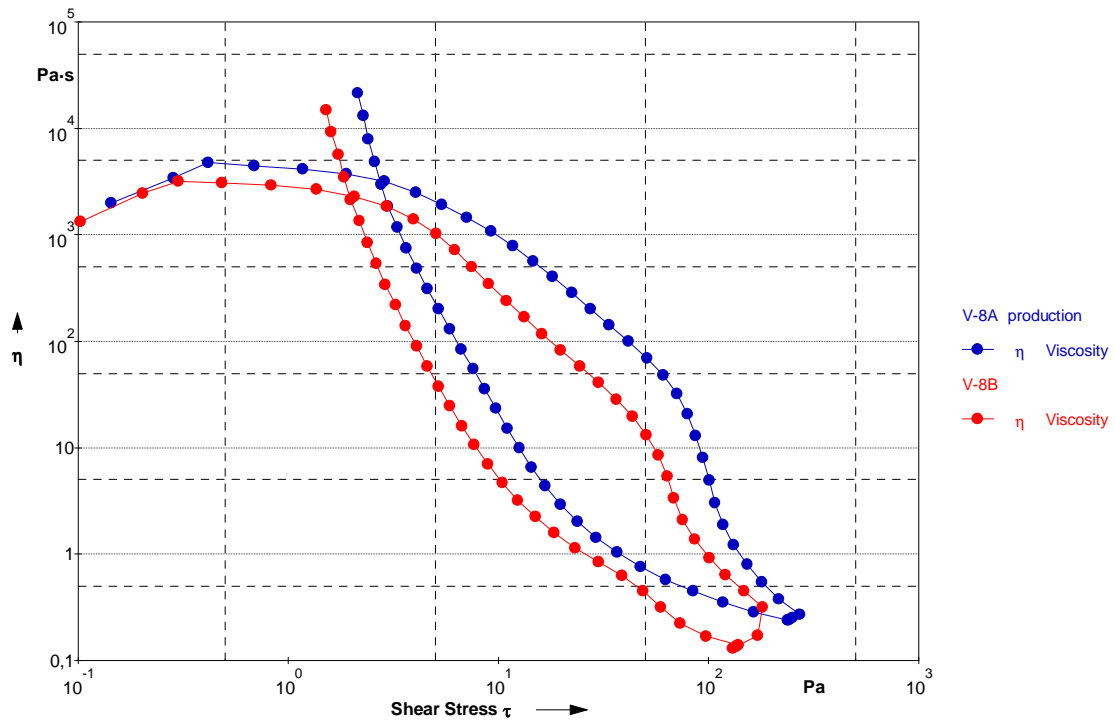
V-6 – We do this sample with a filler paste version V-8, we add the paste after rubbing. The flow curves show different rheological behaviour and in a few days the sample dries out. It seems that this version could not hold water in the system, which makes the system unstable. We try with more water in V-6B and the sample in effect has too low viscosity (Graph 11).



**Graph 12:** Flow curves of the following samples: violet colorant V-6C, V-7A and V-7A after 40 days in the stove at 40°C.

V-6C – We try making a sample with less water and in this way raise viscosity at high shear stress. Viscosity changes but not as much as we would like. We know that we have to change something; the filler paste in the end does not seem to work towards stabilization of the system (Graph 12).

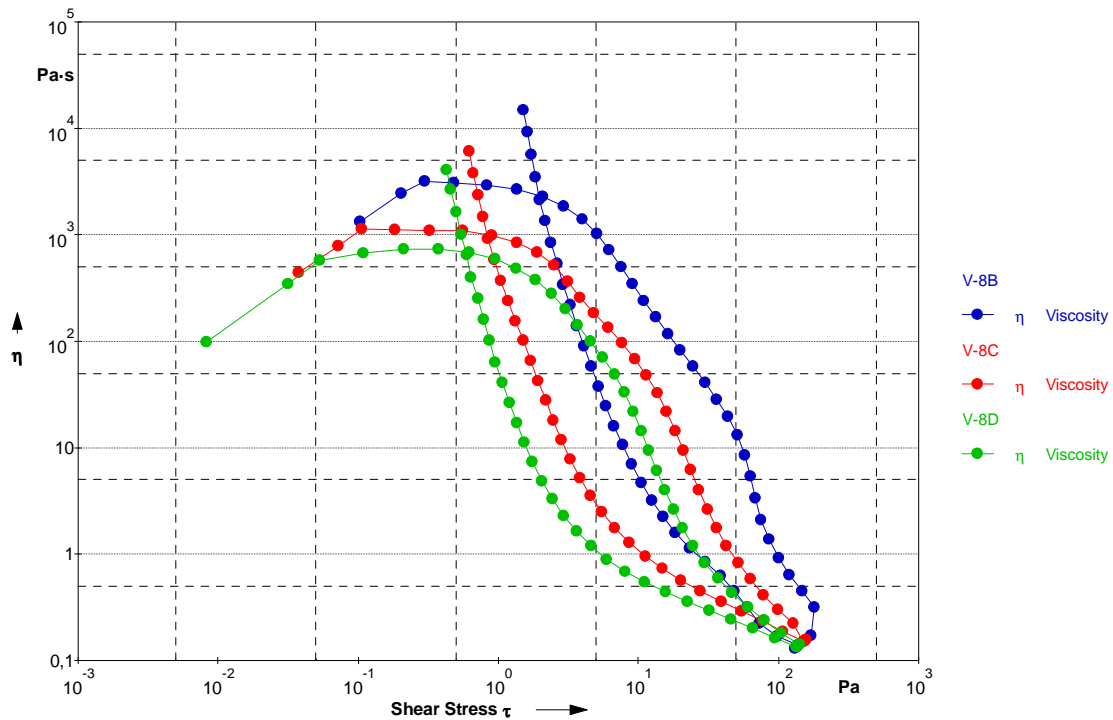
V-7A – We make this sample with the same values of the raw materials as with V6. The difference being only in technology: we put the filler paste version V-8 before rubbing and the sample is stable even after 40 days in the stove (Graph 12).



**Graph 13:** Flow curves of the following samples: violet colorant V-8A and V-8B.

V-8A – This sample is made in the production plant. Monitoring the flow curve ensures that producing the product in the production plant would not be problematic (Graph 13).

V-8B – We take the V-8A sample and add 6.8% of the filler paste version V-8. Viscosity drops - this can be explained with a lower viscosity of the filler paste version V-8. This checking is also useful because it confirms that there is no chemical reaction, only a physical one, while the flow curve is almost the same - it just drops for few values (Graph 13).



**Graph 14:** Flow curves of the following samples: violet colorant V-8B, V-8C and V-8D.

V-8B, V-8C and V-8D samples were used to check the effect that the addition of water or a filler paste has – this checking was necessary because water and filler pastes will have to be added also in production plants when colouristic improvements will be required (Graph 14). There can be differences in the colour strengths among batches and that is why we had to leave some free space in the recipe. We added less water and filler paste in the production plant as by the recipe and we added those two raw materials at the end after the rubbing as much as needed depending on the colour strength.

### 4.1.3. Magenta C.I.: P.R.122

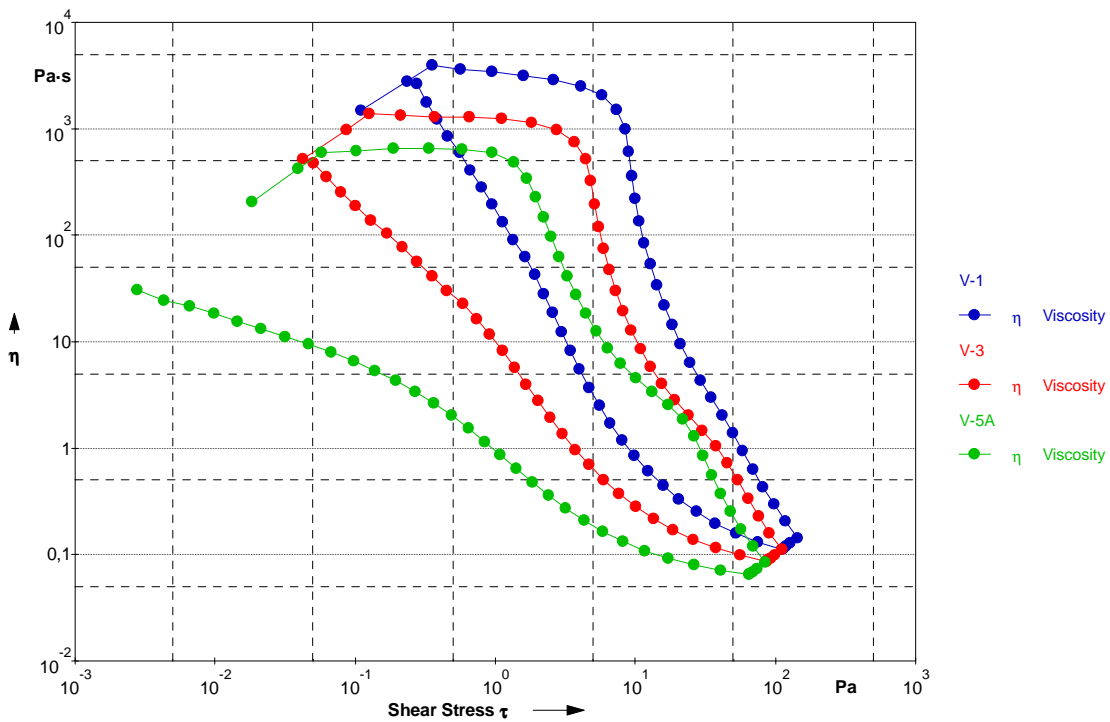
From the point of view of rheological stabilization we find this pigment to be the most problematic. We can tell this from our experience with the already existing colorants with this pigment. We were also checking the rheological flow behaviour of our competitors. Although the measurements show that the colorant should have no problems in the dispensing machine, it appears that after two months the colorant got stuck in the pump of the dispenser. This indicates an increase in the viscosity of the colorant. Another problem is in the increase of the thixotropic flow behaviour. On the flow Graph this is visible at the starting point of the measurements when the flow curve is almost horizontal.

Since we were parallel working also on the colorants we had the first samples on the magenta colorant with the microtalc filler.

**Table 9:** Recipes for magenta colorant from samples V0 to V6.

Version:	V-0 [g]	V-1 [g]	V-2 [g]	V-3 [g]	V-4 [g]	V-5A [g]	V-5B [g]	V-6 [g]
Water	40.0	30.0	30.0	35.0	35.0	40.0	40.0	40.0
Glycerol	5.0	5.0	5.0	5.0	5.0	5.0	5.0	6.0
Defoamer 1	0.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Wetting and dispersing agent 1	10.0	10.0	5.0	10.0	15.0	10.0	10.0	
Wetting and dispersing agent 3								12.0
Dispersing agent 4								0.5
Filler paste version V-4		20.0	25.0	15.0		5.0	5.0	
Filler paste version V-8					10.0			
Pigment: Magenta P.R.122	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
MICROTALC	15.0							
Rubbing 40 minutes								
Water		3.5	4.0	3.5	3.5	9.0	6.0	8.0
Deaerator 1		0.5		0.5	0.5		0.5	0.5
Filler paste version V-8							8.1	2.0
<b>Σ</b>	100.5	100.0	100.0	100.0	100.0	100.0	105.6	100.0

**Rheology results for the magenta colorant flow curves.**

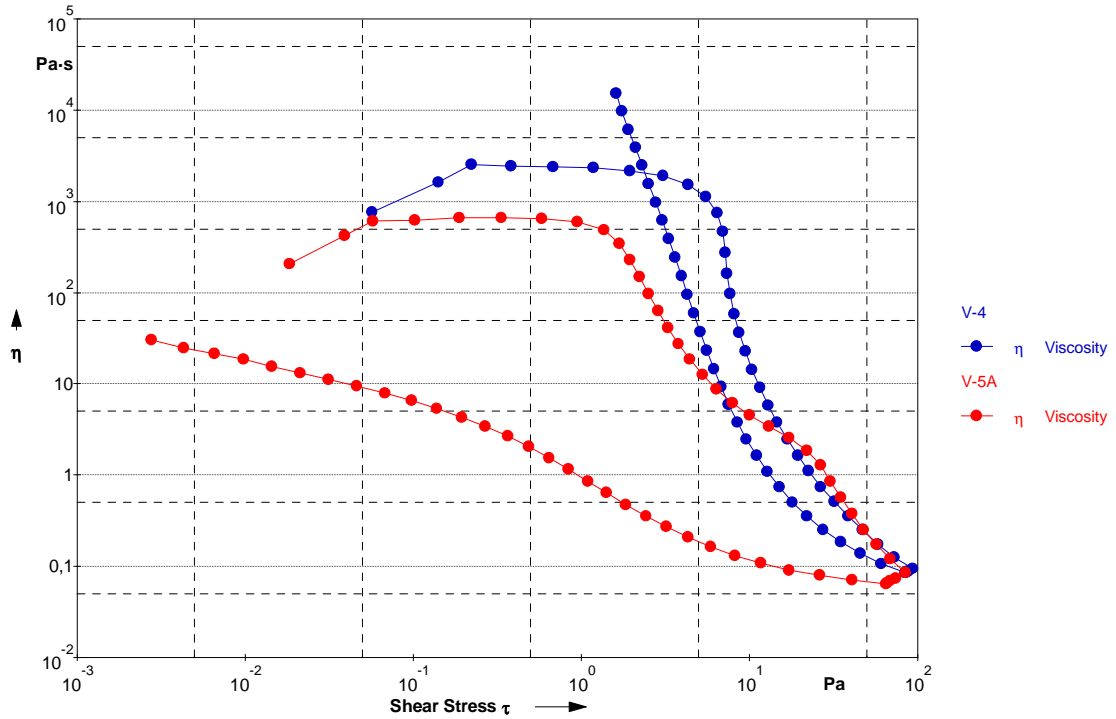


**Graph 15:** Flow curves of magenta colorant V-1, V-3 and V-5A samples.

V-1 – V4 filler paste makes the sample more pseudoplastic. As it can be seen from the graph 15 less filler paste we used less is our sample pseudoplastic and more thixotropic.

V-3 – We increase water in order to make our sample less pseudoplastic only to find out that doing this makes the sample acceptable a few more days but at the end the result was the same as with V-1 (Graph 15).

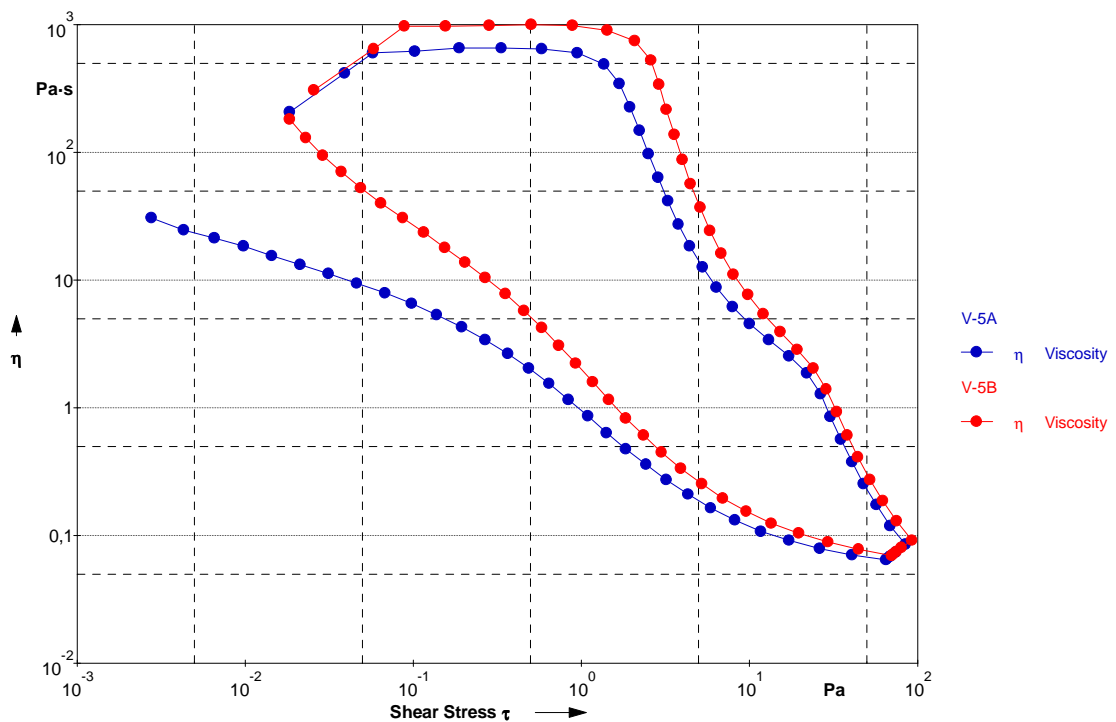
V-5A – We add more water and much less V-4 filler paste. The acceptable quality lasts for 30 days which is a few days longer than with the V-3 sample. This period is far too short since this defect is seen on room temperature.



**Graph 16:** Flow curves of magenta colorant V-4 and V-5A samples.

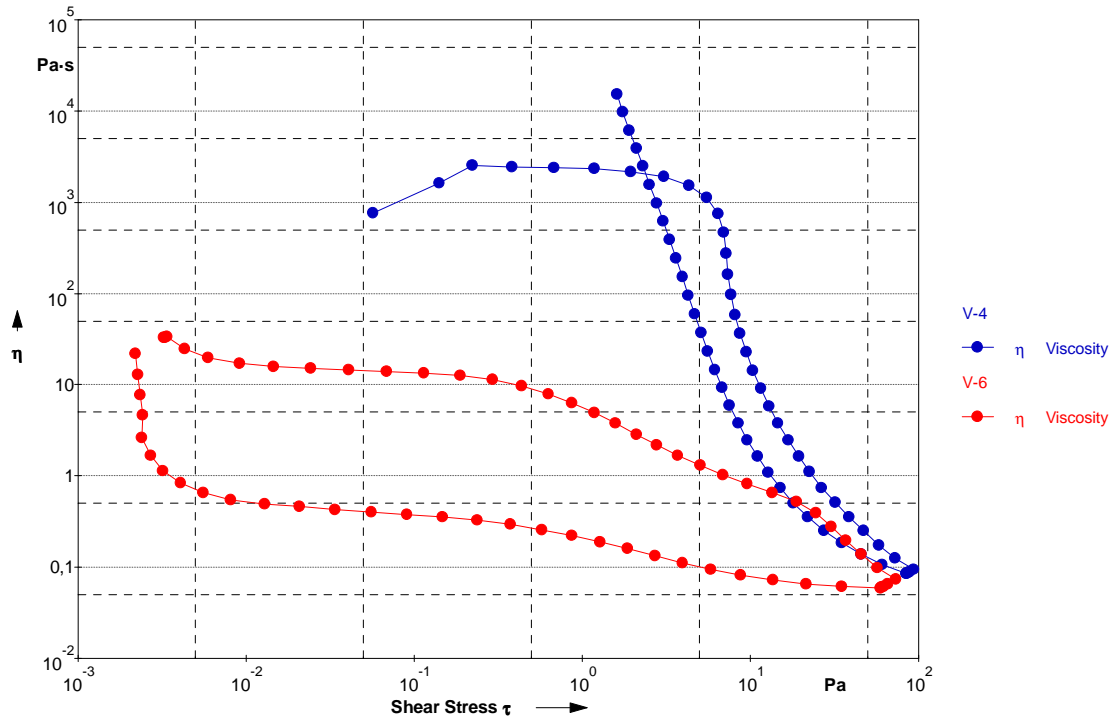
V-4 – We added filler paste V-8 (finntalc). The sample stays stable even after a few weeks no defects were noticed when we stir the sample with a stick (Graph 16).

V-5A – The flow difference is small comparing to V4 (Graph 16).



**Graph 17:** Flow curves of magenta colorant V-5A and V-5B samples.

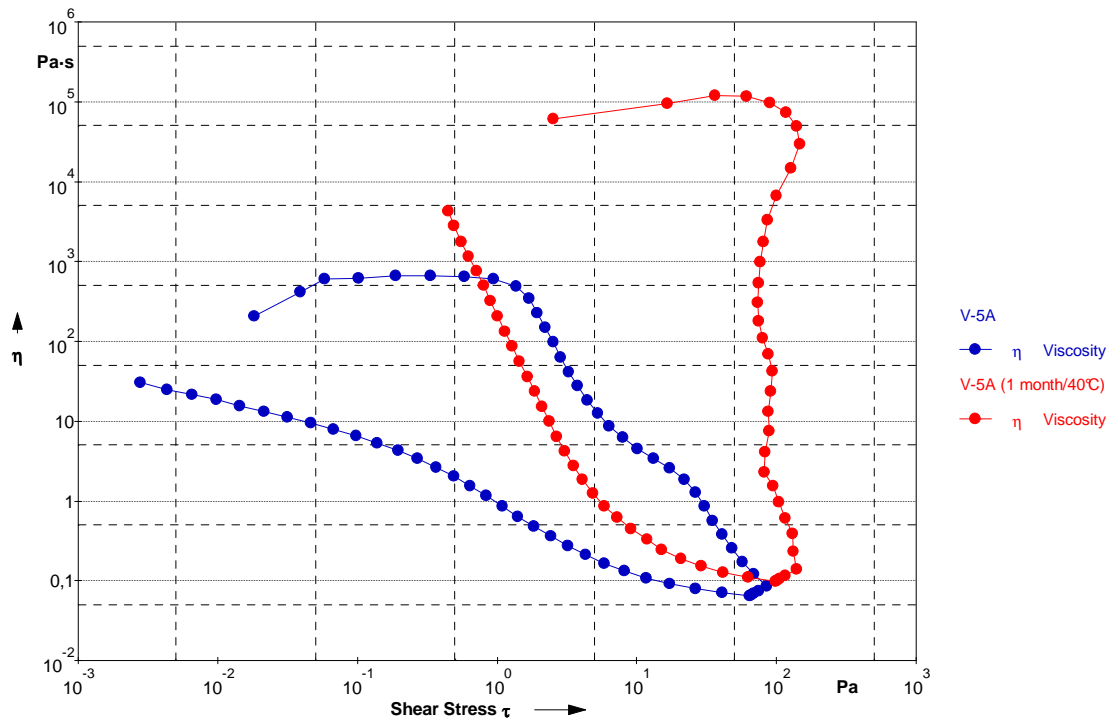
Graph 17 shows no significant differences in rheology behaviour if we vary the quantity of water and the filler paste. This information is valuable since it means that we can use water and the filler past for colouristic control.



**Graph 18:** Flow curves of magenta colorant V-4 and V-6 samples.

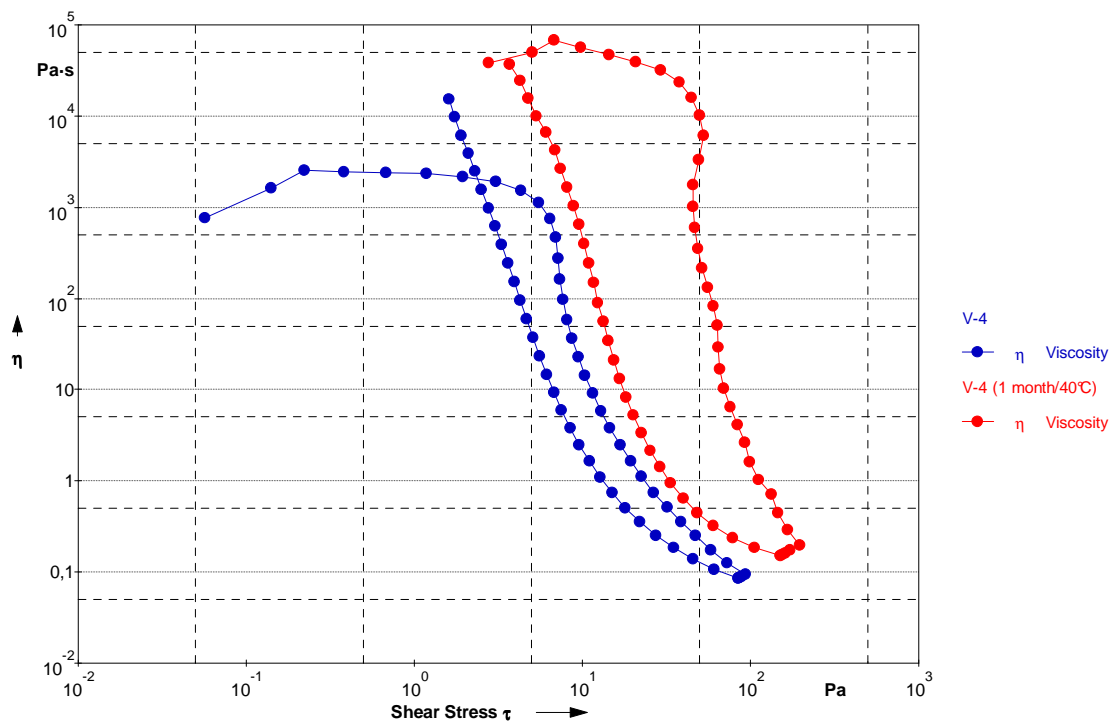
On Graph 18 we can see V-6 which shows different rheological properties as V-4. V-6 is produced without the filler paste in the rubbing stage and with new wetting and dispersing agents.





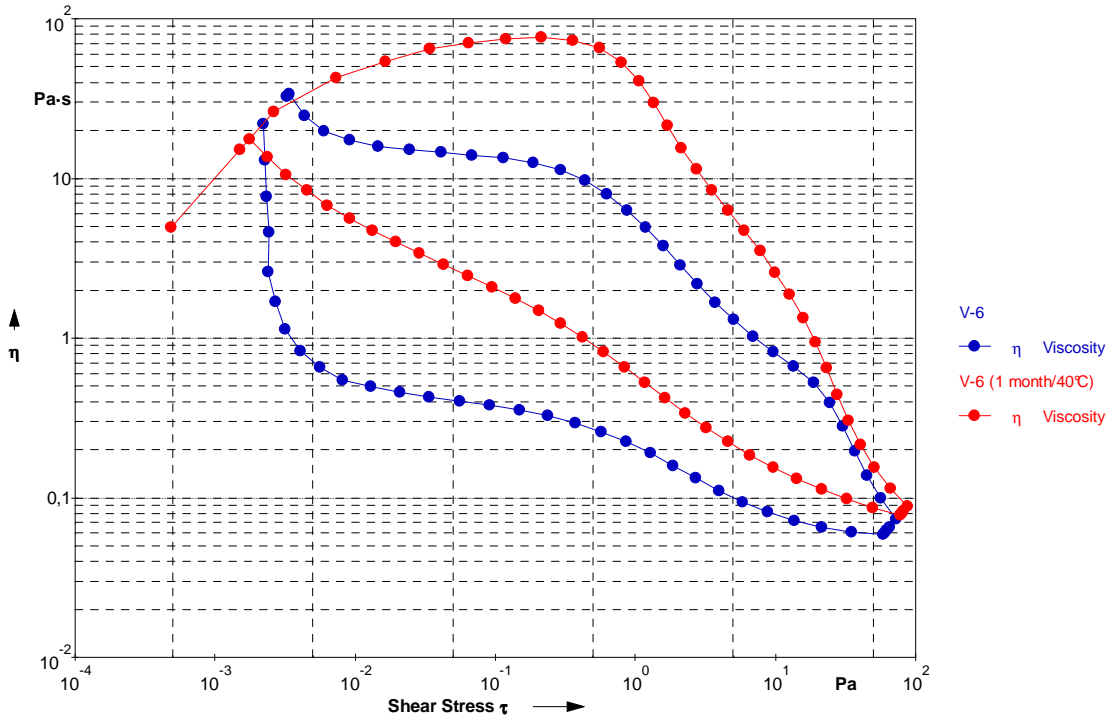
**Graph 19:** Flow curves of samples magenta colorant V-5A and V-5A after 1 month on 40°C.

Differences in the quality between the V-5A sample before its storage in the stove and after is also very evident from the flow curves in Graph 19.



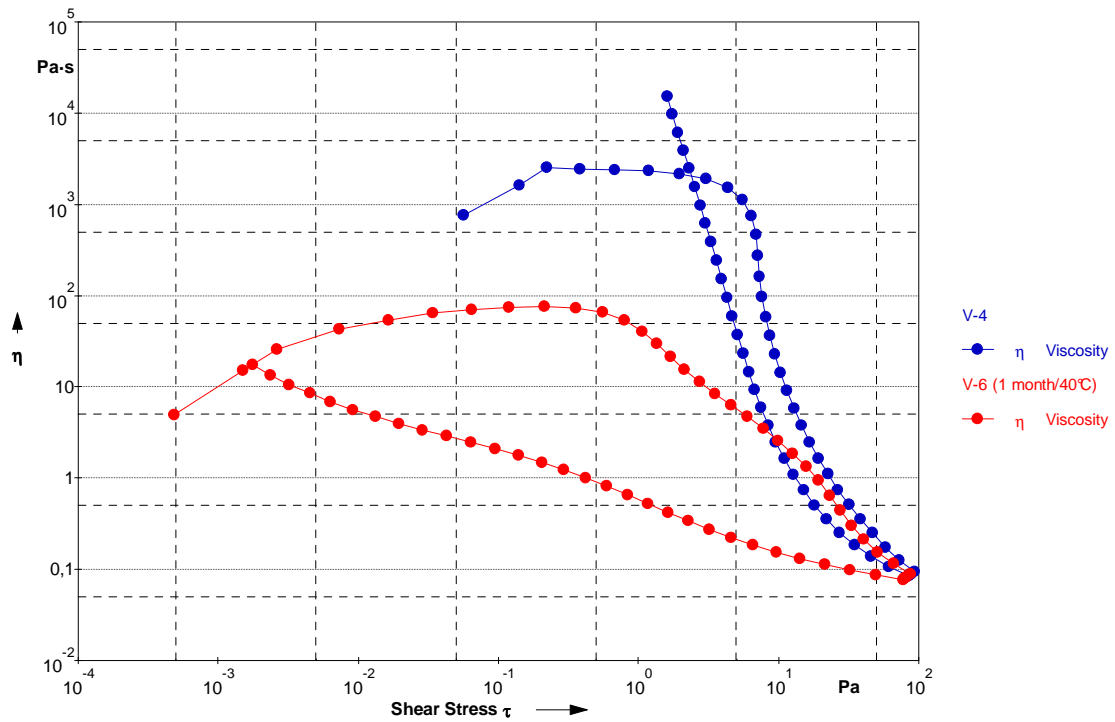
**Graph 20:** Flow curves of magenta colorant V-4 and V-4 samples after 1 month at 40°C.

Graph 20 shows the difference in the flow behaviour after storing the V-4 sample in the stove.



**Graph 21:** Flow curves of samples magenta colorant V-6 and V-6 after 1 month on 40°C.

Graph 21 shows the difference in the flow behaviour after the storage of the V-6 sample in the stove. Viscosity raised but the difference in the flow curves was not so big which confirms that the sample is more or less stable. Sample gets more pseudoplastic but samples shows good stability at the high shear stress.



**Graph 22:** Flow curves of magenta colorant V-4 and V-6 samples after 1 month at 40°C.

The decision which sample is more stable was evident; we decided to confirm V-6 for the production plant since it shows better stability and lower viscosity at 1 Pa shear stress (Graph 22).

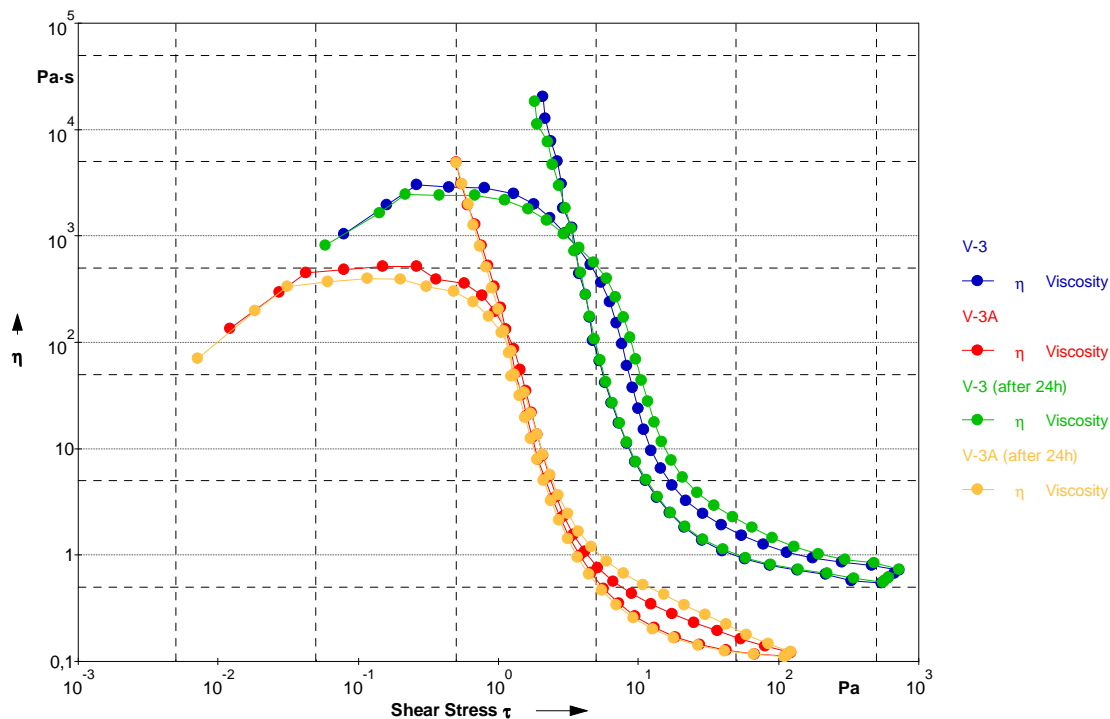
#### 4.1.4. Red oxide C.I.: P.R.101

We were also preparing inorganic red oxide and were performing this with different filler versions. After firstly confirming red oxide colorant V4 we later decided to go with finntalc.

**Table 10:** Recipes of red oxide colorant from sample V1 to V6B.

Version:	V-1 [g]	V-2 [g]	V-3 [g]	V-3A [g]	V-4 [g]	V-5A [g]	V-5B [g]	V-6A [g]	V-6B [g]
Water	28.0	15.0	15.0	20.0	15.3	8.0	8.0	8.0	8.0
Glycerol	7.5	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Wetting and dispersing agent 3	0.9								
Wetting and dispersing agent 1	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Dispersing agent 2			0.7	0.7	0.7	1.5	1.5	0.7	0.7
Pigment: Red oxide P.R.101	61.0	61.0	61.0	61.0	61.0	61.0	61.0	61.0	61.0
Defoamer 1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.5	0.5
Dispersing agent 4		0.3							
Filler past version V-8						15.0	15.0	16.0	16.0
MICROTALC	5.0	2.0	7.5	7.5	9.0				
Rubbing 40 minutes									
Water					3.0	4.0		4.0	
Filler past version V-8							4.0		4.0
Deaerator 1			0.2	0.2	0.2				
<b>Σ</b>	108.4	89.3	95.4	100.4	100.2	100.5	100.5	100.2	100.2

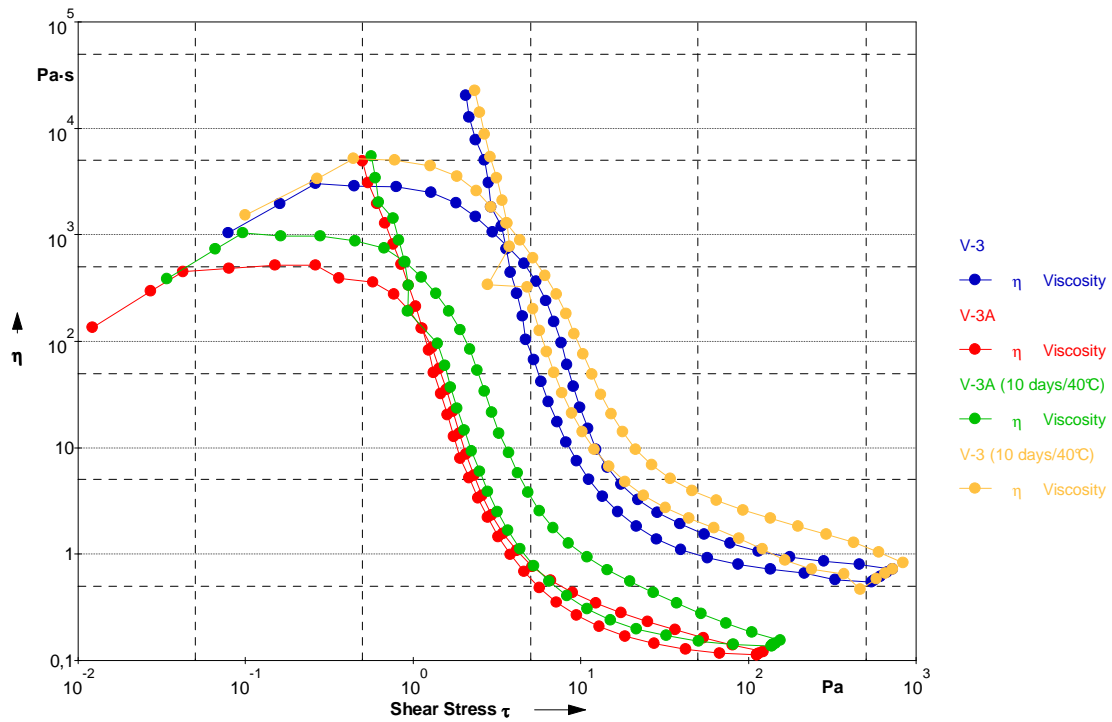
**Rheology results for the red oxide colorant flow curves.**



**Graph 23:** Flow curves of samples red oxide colorant V-3, V-3A.

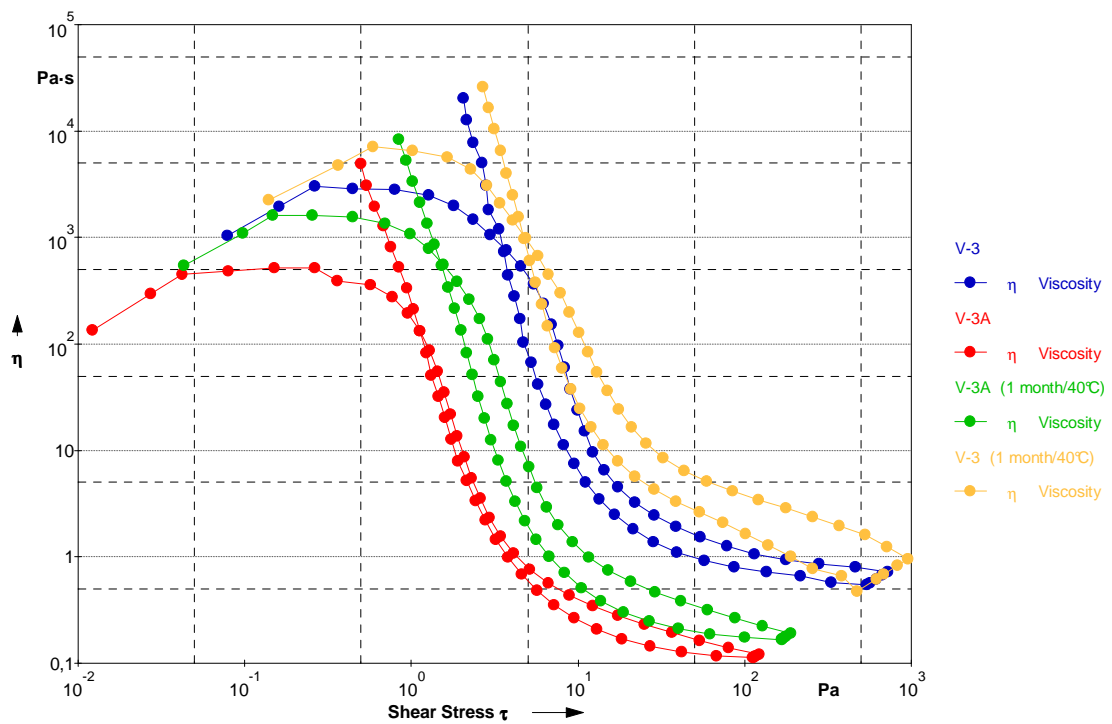
V-3 – We have Wetting and dispersing agent 1 and Dispersing agent 2. We also check the differences in the flow curves of the flow tests done immediately and after 24 hours. We can conclude that there is no significant difference. Viscosity is too high (Graph 23).

V-3A – We add more water which decreases the viscosity (Graph 23).



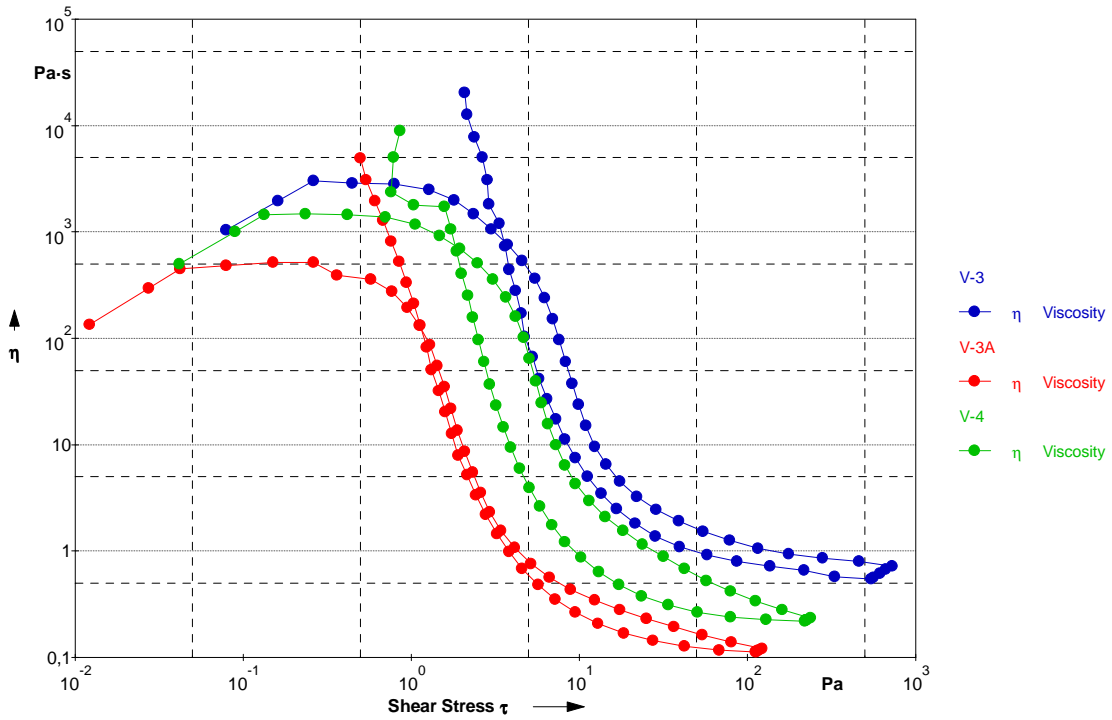
**Graph 24:** Flow curves of samples red oxide colorant V-3, V-3A. After 10 days.

The difference between the samples (V-3 and V-3A) was small, that also shows graph 24. For both samples we can say that they are still stable after 10 days in the stove at 40°C.



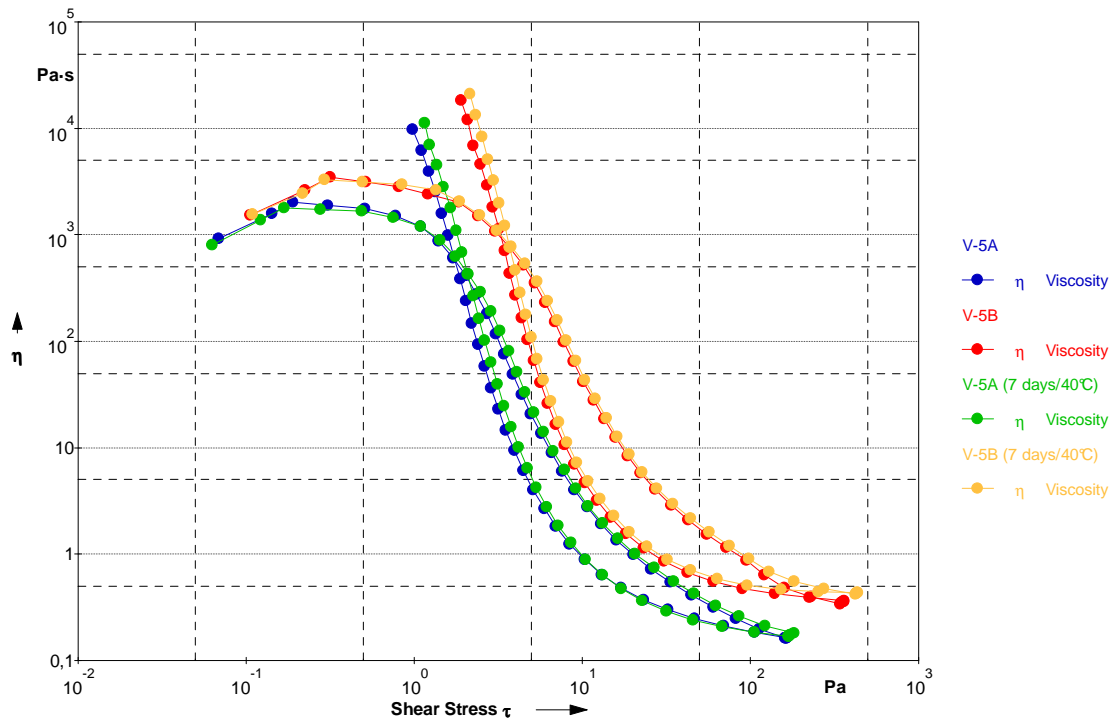
**Graph 25:** Flow curves of samples red oxide colorant V-3, V-3A. After 1 month.

For both samples we can confirm that after 1 month in the stove at 40°C they are still stable (Graph 25). The V-3 sample shows higher viscosity at high shear stress which could mean problems in a dispensing machine (e.g. difficult dispensing).



**Graph 26:** Flow curves of samples red oxide colorant V-3, V-3A and V-4.

V-4 – This sample consists of less water and more microtalc. It has proved to be acceptable with the viscosity we want at high shear stress. We find V-3 with too high and V-3A with too low viscosity (Graph 26).

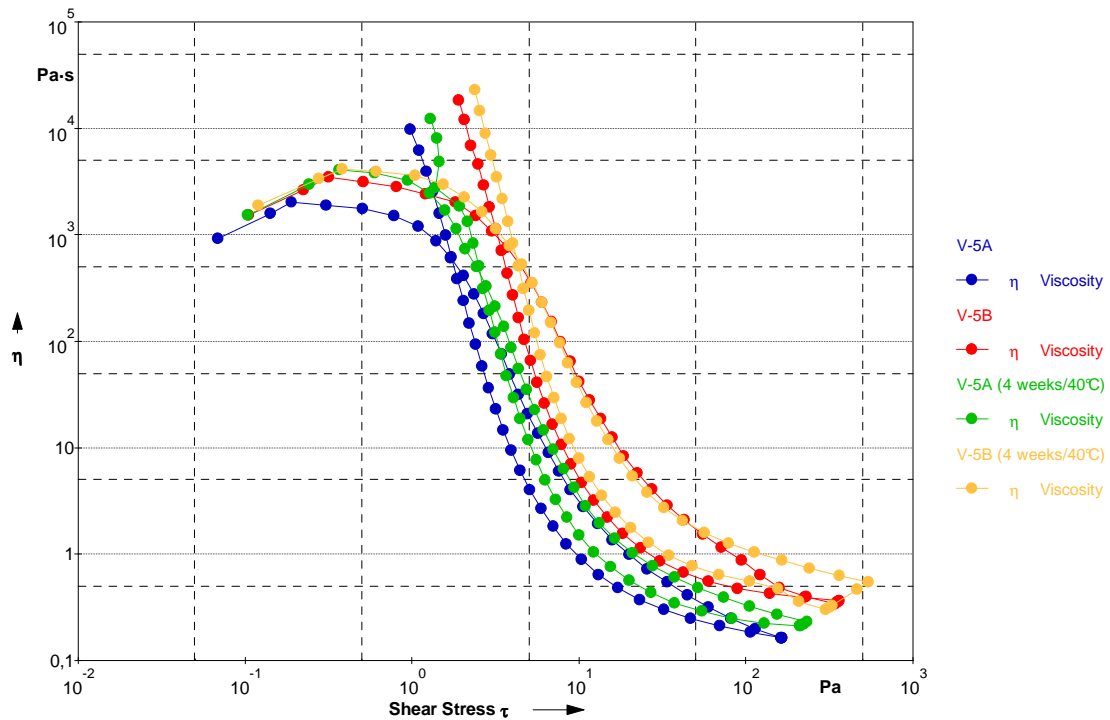


**Graph 27:** Flow curves of samples red oxide colorant V-5A, V-5B after 7 days.

V-5A – This sample in combination with the V-8 filler paste shows a very good stabilization after 7 days. It has 5 % more water than the V-5B sample (Graph 27).

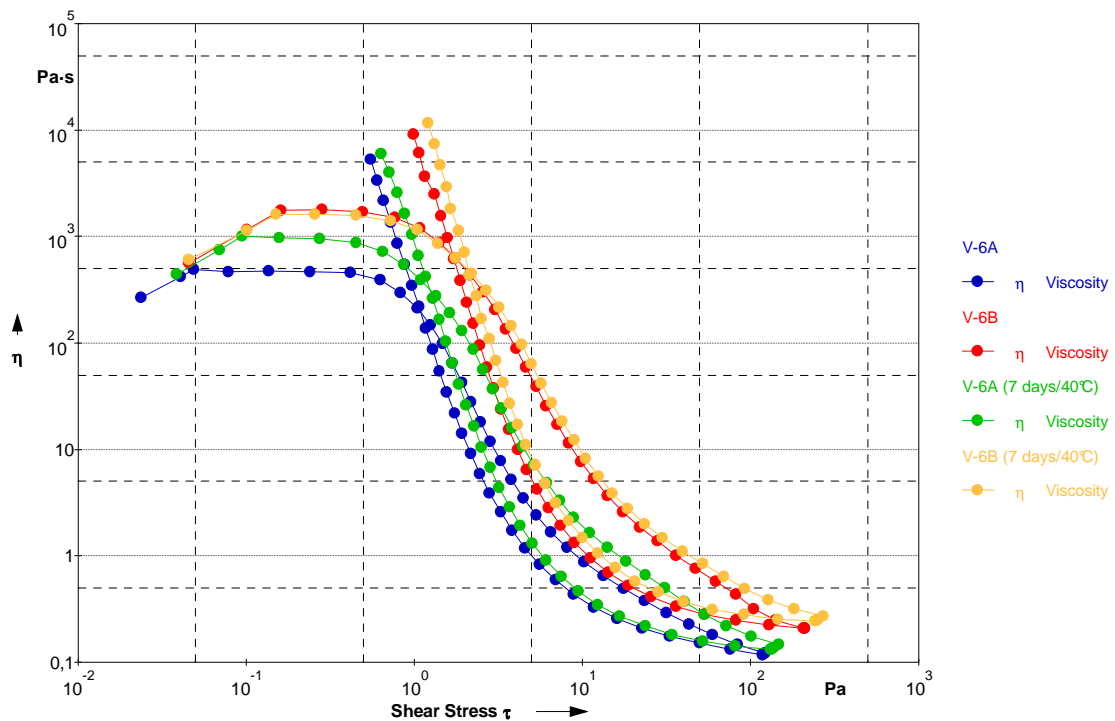
V-5B – This sample in combination with the V-8 filler paste shows a very good stabilization after 7 days. It has 5 % more V-8 filler paste than the V-5A sample. The difference is evident in a higher viscosity than in the V-5A sample which is logical since more filler paste increases the solid matter (Graph 27).





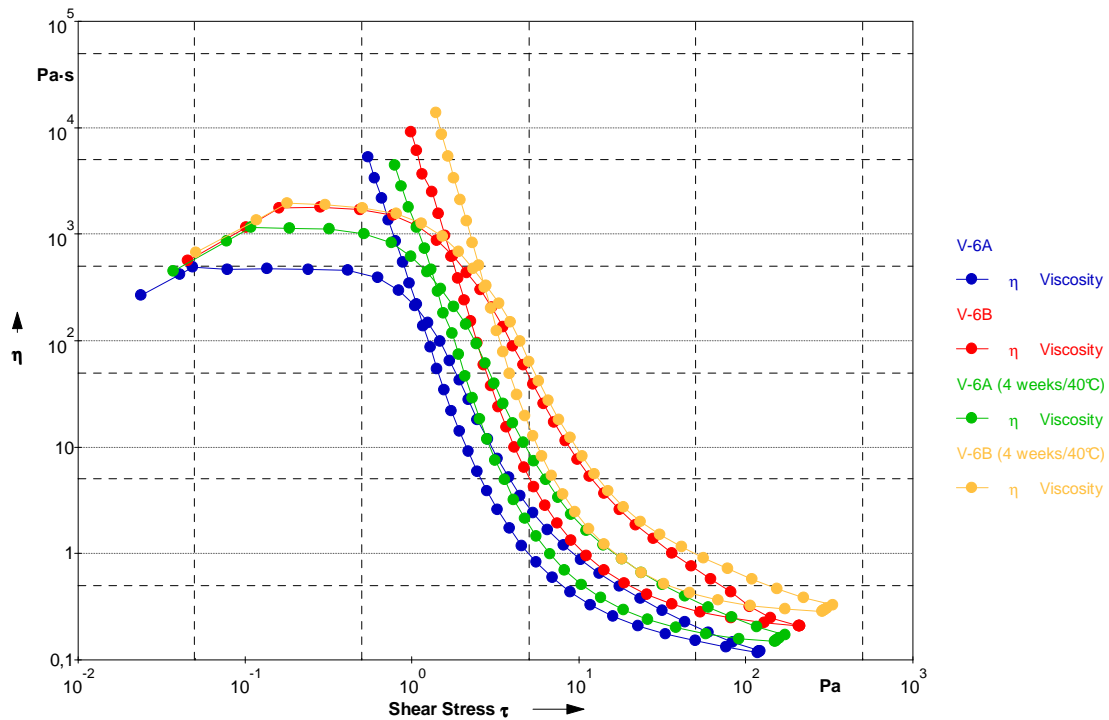
**Graph 28:** Flow curves of samples red oxide colorant V-5A, V-5B. After 4 weeks.

Graph 28 shows less differences in flow curves for the V-5A sample. Both samples are still stable but from the flow test we can decide that V-5A is more stable.



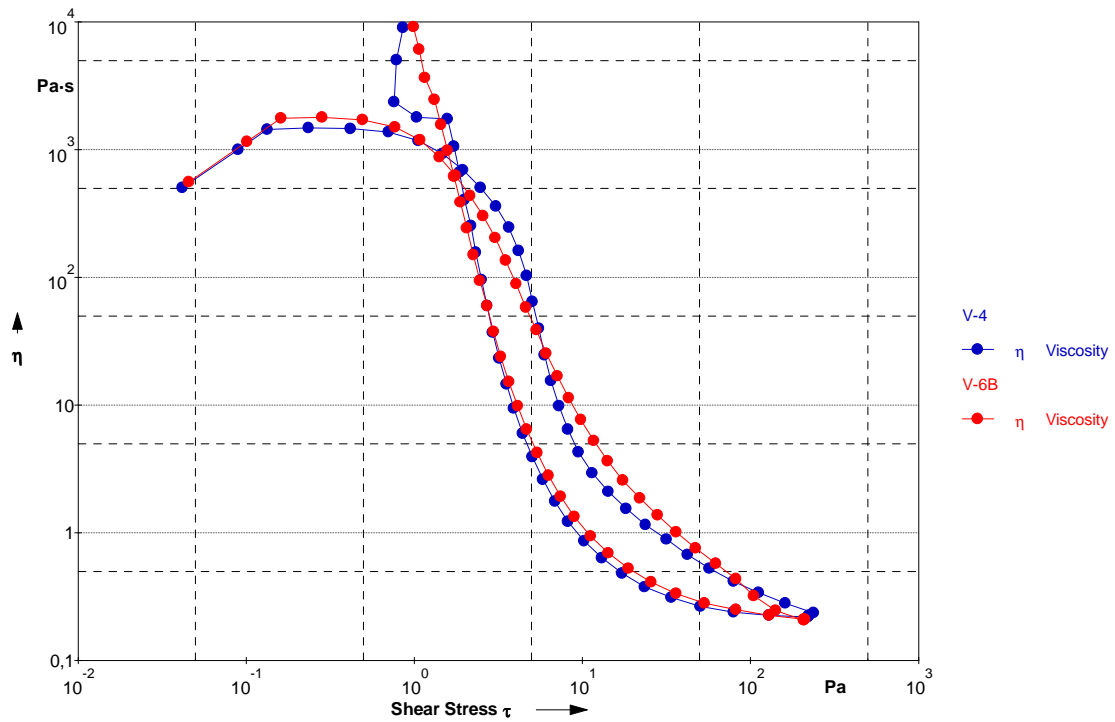
**Graph 29:** Flow curves of samples red oxide colorant V-6A, V-6B. After 7 days.

V-6A and V-6B have 0.8 % less dispersing agent 2 because of a cheaper recipe. Flow Graph 29 shows good stabilization also after 7 days.



**Graph 30:** Flow curves of samples red oxide colorant V-6A, V-6B after 4 weeks.

Graph 30 reveals good stability of samples V-6A and V-6B also after being 4 weeks in the stove. It is better to have viscosity at high shear stress with the 6-A than with the V-6B sample. If viscosity for this colorant is too low this can mean too much dropping in the dispenser. The density is high which means it is easier to form the drop at low viscosity.



**Graph 31:** Flow curves of samples red oxide colorant V-4 and V-6B.

As we find V-4 very stable we were also very satisfied that we had managed to prepare a sample V-6 with the V-8 filler paste with almost the same rheology properties (Graph 31).

#### 4.1.5. Hybrid orange pigment

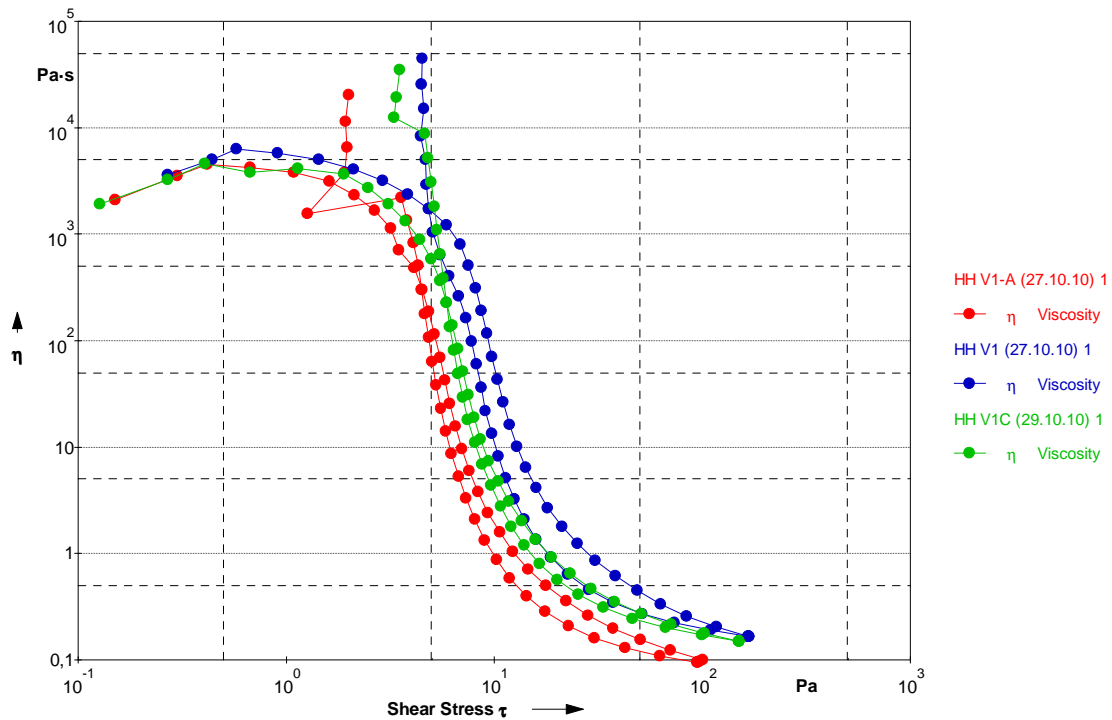
**Table 11:** Recipes of the orange colorant from sample V1 to V5.

Version:	V-1 [g]	V-1A [g]	V-1C [g]	V-2 [g]	V-3 [g]	V-4 [g]	V-5 [g]
Water	35.0	35.5	35.0	30.0	30.0	40.0	35.0
Glycerol	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Defoamer 1	1.0	1.0	1.0		1.0	1.0	1.0
Defoamer 3							
Defoamer 4				1.0			
Wetting and dispersing agent 1	10.2	13.0	13.0	10.2	10.2	5.0	5.0
Dispersing agent 2	0.5	1.5	1.5	0.5	0.5		
Wetting and dispersing agent 5						0.3	0.3
Dispersing agent 4							
MICROTALC	5.0	5.0	5.0				
Filler past version V-8				10.0	10.0	5.0	10.0
Pigment	38.0	38.0	38.0	38.0	38.0	38.0	40.0
Rubbing 40 minutes							
Defoamer	0.3	0.3	0.8	0.3	0.3	0.3	1.0
Water							
Filler paste version V-8							
<b>Σ</b>	95.0	99.3	99.3	95.0	95.0	94.6	97.3

**Table 12:** Recipes of the orange colorant from sample V6 to V11.

Version:	V-6 [g]	V-7 [g]	V-8A [g]	V-8B [g]	V-9 [g]	V-10 [g]	V-11 [g]
Water	30.0	35.0	35.0	35.0	30.0	26.0	23.0
Glycerol	5.0	5.0	5.0	5.0	6.0	8.0	7.0
Defoamer 1		1.0	1.0	1.0	1.0	1.0	1.0
Defoamer 3	1.0						
Defoamer 4							
Wetting and dispersing agent 1	5.0	5.0	5.0	5.0	10.0		
Dispersing agent 3						15.0	15.0
Dispersing agent 2			0.5	0.5	5.0		
Wetting and dispersing agent 5	0.3	0.3	0.3	0.3			
Dispersing agent 4						0.2	0.2
MICROTALC							
Filler past version V-8	10.0	5.0	10.0	10.0	5.0	5.0	10.0
Pigment: Hybrid orange	40.0	40.0	40.0	40.0	40.0	40.0	40.0
40 minutes of rubbing							
Defoamer 2			0.5	0.5		0.50	0.50
Water			3.2				
Filler paste version V-8				3.2		4.30	3.30
<b>Σ</b>	91.3	91.3	100.5	100.5	97.0	100.0	100.0

## Rheology results for the orange colorant flow curves.

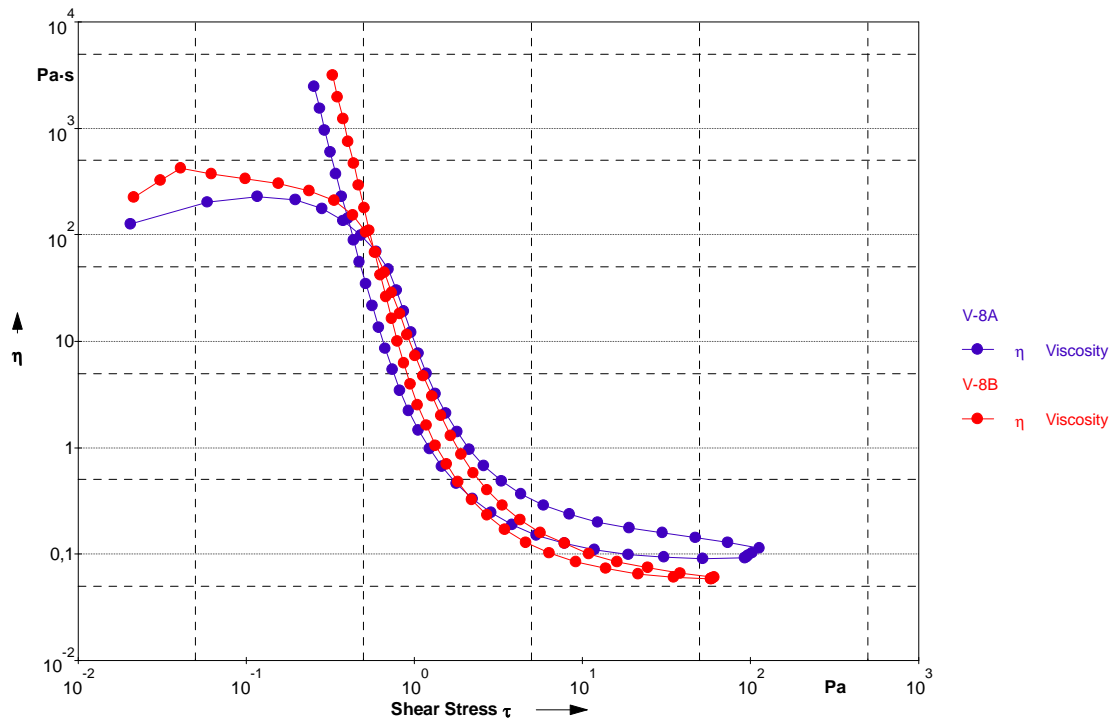


**Graph 32:** Flow curves of samples orange colorant V-1, V-1A and V-1C.

V-1 – This is the first version of the orange colorant. While rubbing the colorant, we notice that too much force was required to rub the paste.

V-1A – We add Wetting and dispersing agent 1 and Dispersing agent 2. The rubbing of this colorant is much easier and the flow curve shows a difference in viscosity at high shear stress (Graph 32).

V-1C – We add more deaerator to see if microfoam is present. From the flow test on Graph 32 we can see the difference but it is very difficult to say if this difference has been measured because of the defoamer. However the difference in density is 0.02 g/l which is very little. Therefore we decide that adding more deaerator 2 in the end is not necessary.

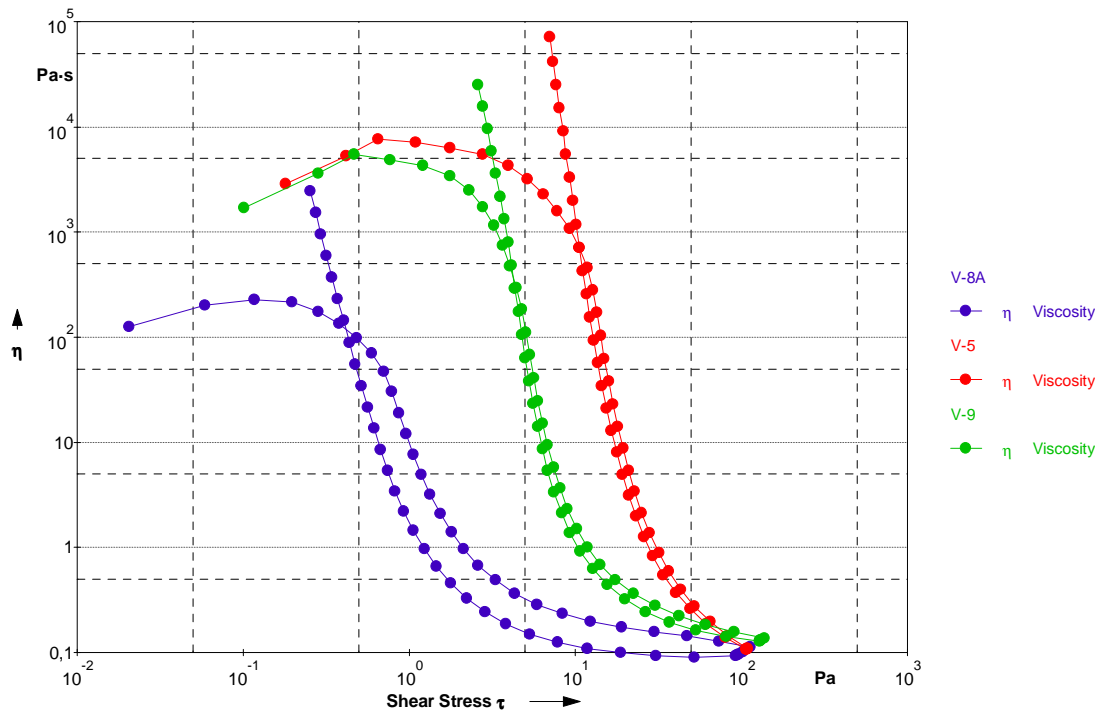


**Graph 33:** Flow curves of samples orange colorant V-8A and V-8B.

V-8A – Before this version we were looking for a different defoamer and dispersing agent, however in the end we returned to the known Defoamer 1 and Deaerator 1. We add a new Dispersing agent 4 and Wetting and dispersing agent 5 which we think helps us get a stable system (Graph 33).

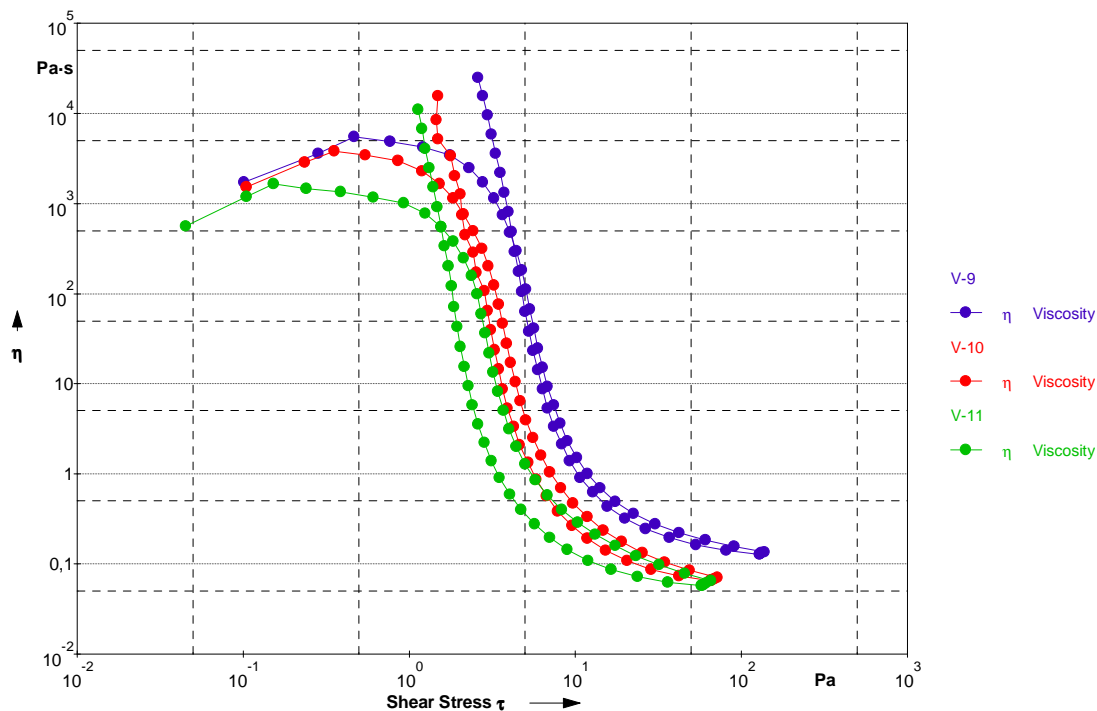
V-8B – This version has 3.2 % of the V-8 filler paste more than V-8A which has more water.

From Graph 33 we can assume that V-8B is more stable therefore we made new versions with different volumes of the filler paste and some other raw materials.



**Graph 34:** Flow curves of the following samples: orange colorant V-5, V-8A and V-9.

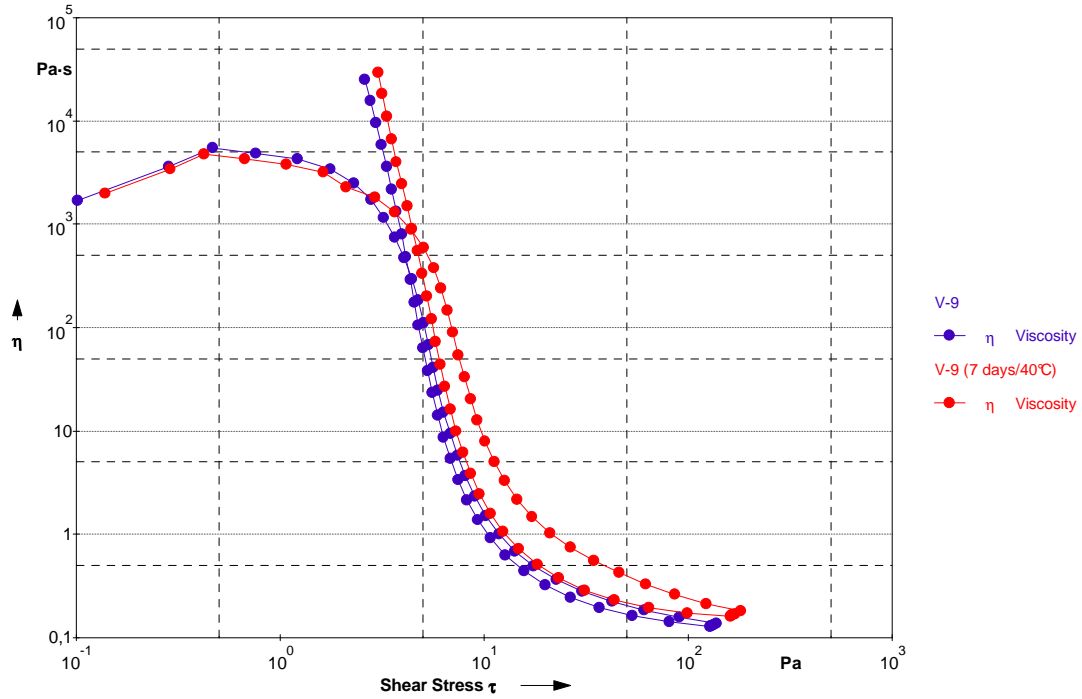
Graph 34 shows three different samples from which V-8A is the most stable - it shows lower value of viscosity at low shear stress. The V-9 sample is still acceptable in practical use (checked by stirring with a stick). The V-5 sample is not acceptable because its pseudoplastic behaviour is too strong (stirring this sample with a stick was hard).



**Graph 35:** Flow curves of the following samples: orange colorant V-9, V-10 and V-11.

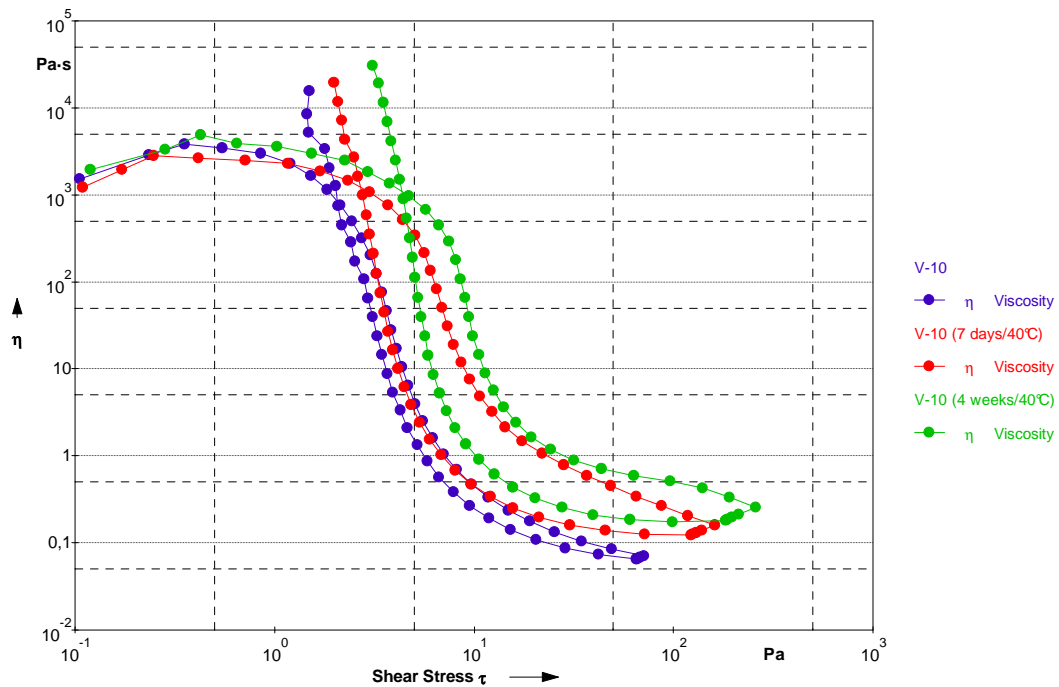


Graph 35: Taking into account the cheaper recipe we made some new samples which were more like V-9. It was good that we prepared the samples with a lower viscosity.



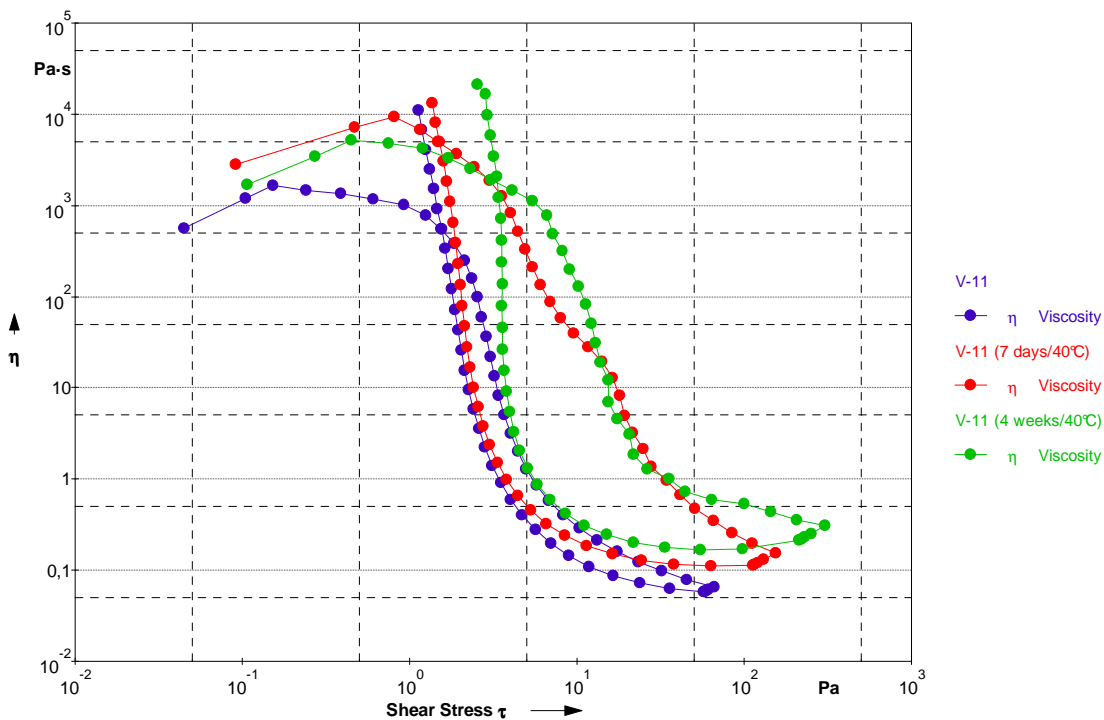
**Graph 36:** Flow curves of sample orange colorant V-9 after 7 days in the stove.

V-9 – The sample is not stable for more tests. Its viscosity at low shear stress increases and therefore a normal use of the colorant is no longer possible (Graph 36).



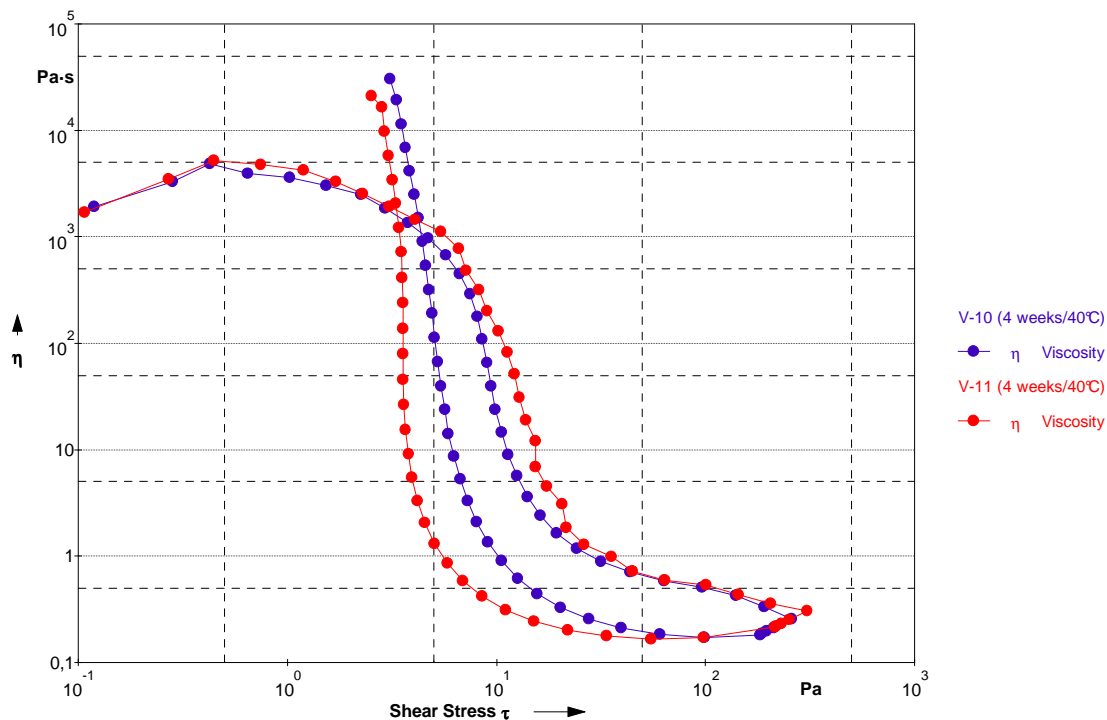
**Graph 37:** Flow curves of the V-10 samples after 7 days and 4 weeks in the stove.

Graph 37 for V-10 shows a stable system even after 4 weeks in the stove. From the flow curves we can see the increasing viscosity. What is also evident from the flow curves is their pointing at the same shear stress and a higher diversity when the sample is older. This indicates possible future stability problems of the sample but we cannot predict the exact time they would happen. What we do know is that when a sample shows properties and enables use even after 4 weeks in the stove at below 40°C, the use of such a sample will still be possible after one year in the dispenser, where conditions should be from 20 to 25°C.



**Graph 38:** Flow curves of the orange colorant V-11 samples after 7 days and 4 weeks in the stove.

V-11 – The sample was stable and the use of the sample was possible also 4 weeks after the sample was tested for 4 weeks in the stove. However flow curves suggest possible future problems with this sample. At the higher shear stress the viscosity is starting to rise up that kind of behaviour is usual for rheopectic samples (Graph 38).



**Graph 39:** Flow curves of the orange colorant V-10 and V-11 samples after 4 weeks in the stove.

The flow curves in Graph 39 show measurements of the samples after 4 weeks in the stove at 40°C. We can determine from the curves that the V-10 sample shows a more stable system and for this reason it has been chosen for forward testing.

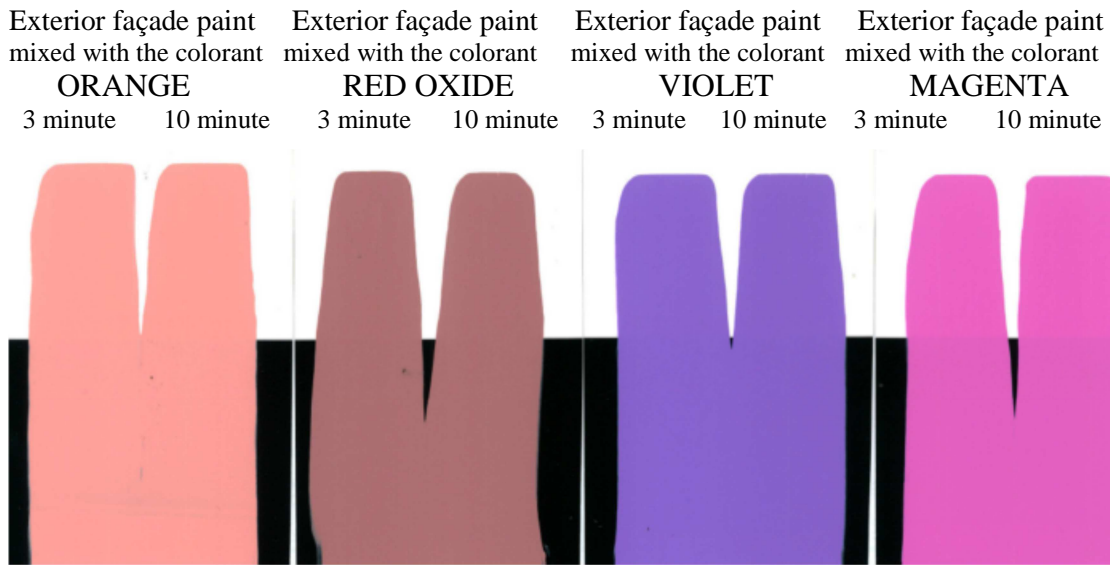
## 4.2. Colorant in waterborne products

We test the colorants in two waterborne paints: Interior wall paint VOC-free and Exterior facade paint (up to 40 g/l VOC). Important tests included the following: wetting test, compatibility test and test with more than one colorant (in our case four).

These two products (paints) have 3 bases: B1, B2 and B3. The VOC-free B1 interior wall paint has 9 % of TiO<sub>2</sub> – white pigment; B2 has 5 % of TiO<sub>2</sub> – white pigment; B3 has 0 % of TiO<sub>2</sub> – white pigment. Exterior facade paint B1 has 12 % of TiO<sub>2</sub> – white pigment; B2 has 3.6 % of TiO<sub>2</sub> – white pigment; B3 has 0 % of TiO<sub>2</sub> – white pigment. The B1 base is used for light shades, B2 for darker shades and B3 for very dark shades.

For this work we only test the colorants in B1 bases. In these two bases we put 3 % of the colorant which is an average dosage in such a base.

The wetting tests with all the samples (VIOLET, MAGENTA, RED OXIDE and ORANGE colorants) were good in the exterior facade paint (Figure 29) and in the interior wall paint (Figure 31). There were no differences among those samples shaken for 3 minute and those for 10.



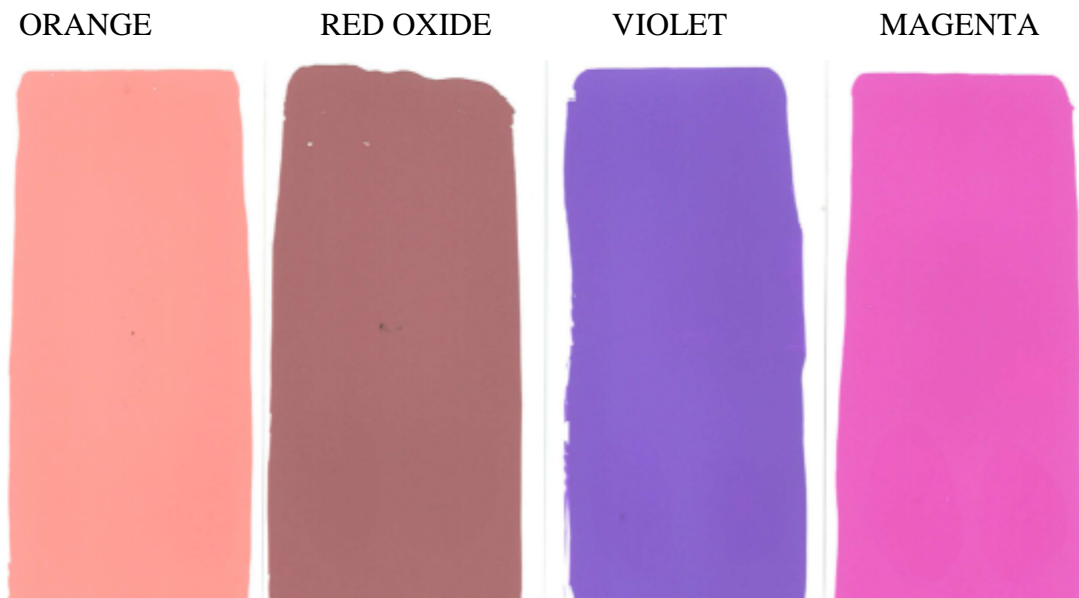
**Figure 29:** Wetting test with the Exterior facade paint and our samples (universal colorants)..

**Table 13:** Results of CIE-lab measurements of the samples from Figure 29.

CIE L*a*b* Colour Difference for exterior facade paint with colorants								
Colorants	DL*	Da*	Db*	DC*	DH*	DE*	CMC-DE	C. strength
ORANGE	0.05	0.07	0.01	0.06	-0.02	0.08	0.05	99.72 %
RED OXIDE	-0.01	0.03	0.03	0.04	0.02	0.04	0.03	100.13 %
VIOLET	-0.01	0.03	-0.04	0.05	0.00	0.05	0.02	100.05 %
MAGENTA	0.01	0.02	0.09	-0.01	0.09	0.09	0.05	100.00 %

Results in Table 13 show the colour differences among the samples shaken for 3 minutes and those shaken for 10 minutes. In these measurements the part of the sample which was shaken for 3 minutes was taken as the standard. All the measurements of colour differences were performed using equipment (Datacolor

Spectraflash SF 600 PLUS Figure 20). As can be seen from Figure 29, there are no differences visible to the eye among samples which are shaken for 3 minutes from those shaken for 10 minutes. A small difference can be detected only with instruments, but this is not an outcome of a real dissimilarity between the samples, because such a small variation is also possible when the measurements are done in different places on the same sample (Table 13).



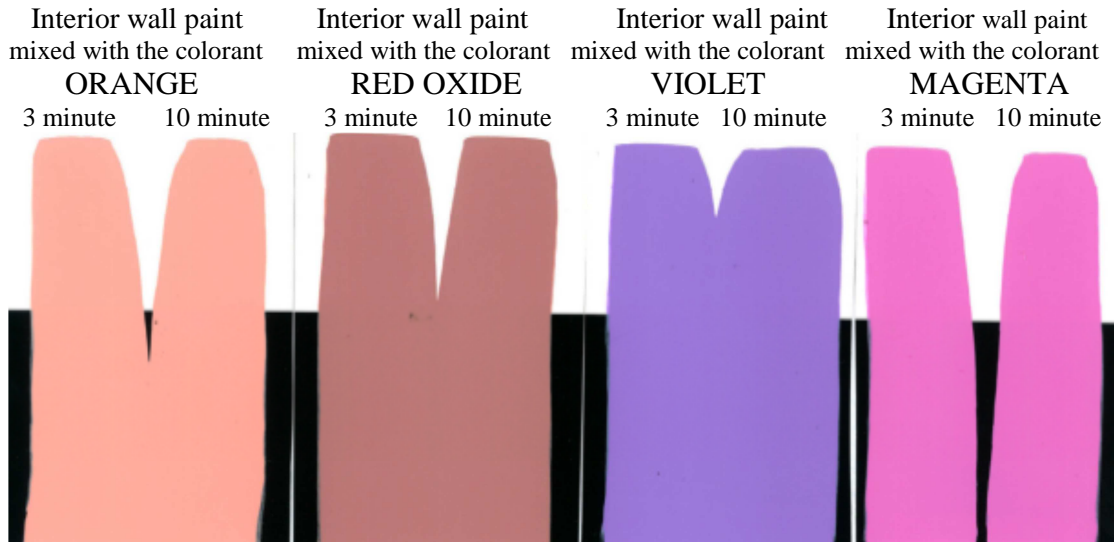
**Figure 30:** Waterborne Exterior facade paint and our samples universal colorants (rub-out test).

**Table 14:** Results of CIE-lab measurements of the samples from Figure 30.

CIE L*a*b* Colour Difference for exterior facade paint with colorants difference in rub out circle								
Colorants	DL*	Da*	Db*	DC*	DH*	DE*	CMC-DE	C. strength
ORANGE	-0.22	0.17	0.48	0.39	0.32	0.55	0.36	103.28 %
RED OXIDE	-0.45	0.35	0.54	0.52	0.38	0.79	0.60	104.35 %
VIOLET	-0.59	0.62	-0.42	0.66	0.35	0.95	0.64	104.09 %
MAGENTA	-0.04	-0.03	0.02	-0.04	0.01	0.05	0.04	100.26 %

Compatibility test (Figure 30) confirmed instrument measurements in Table 14. The results demonstrate good compatibilities of all the colorants in B1 exterior façade paint.

It can be stated for all the four samples that the wetting test shows good compatibility and that there is no wetting problem between the base and the colorants after they are mixed together (the colour strength is the same when the sample is being mixed for 3 minutes or for 10 minutes).

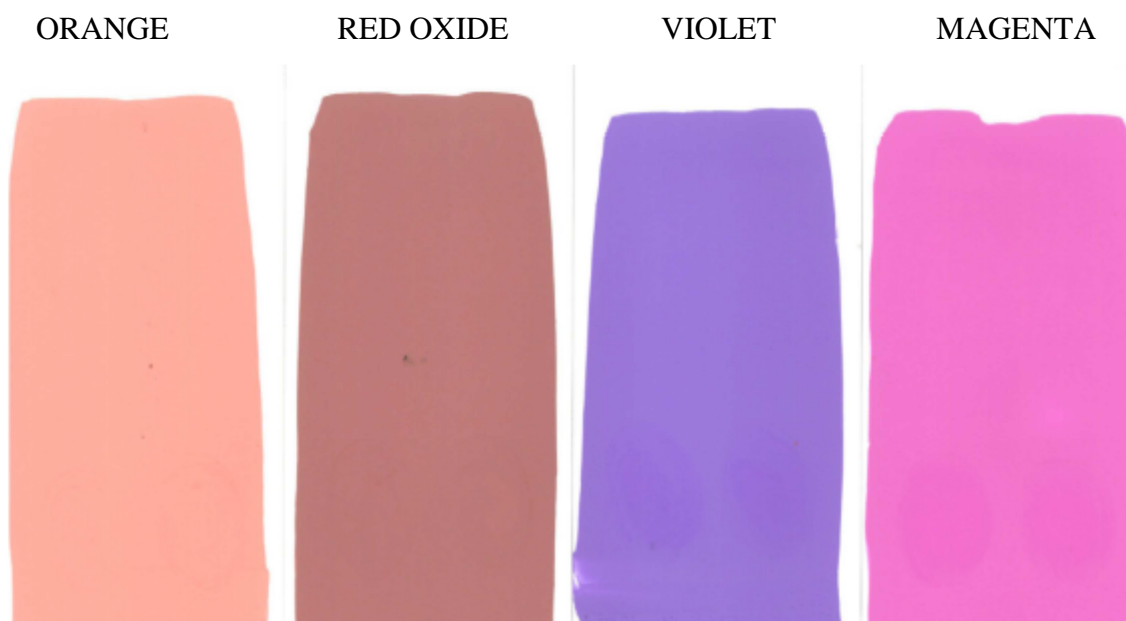


**Figure 31:** Wetting test with Interior wall paint and our samples (universal colorants).

**Table 15:** Results of CIE-lab measurements of the samples from Figure 31.

CIE L*a*b* Colour Difference for interior wall paint with colorants								
Colorants	DL*	Da*	Db*	DC*	DH*	DE*	CMC-DE	C. strength
ORANGE	0.07	-0.09	-0.02	-0.08	0.03	0.11	0.07	99.30 %
RED OXIDE	0.04	0.01	0.00	0.01	0.00	0.04	0.04	99.71 %
VIOLET	0.02	0.07	-0.10	0.12	0.01	0.12	0.06	99.81 %
MAGENTA	0.03	-0.11	0.05	-0.12	0.00	0.13	0.06	99.69 %

Table 15 lays out results which can also be seen in Figure 31. The wetting test with all the four colorants shows good results in the interior wall paint. This means that the colorants can be employed for preparing shades in this product (interior wall paint).



**Figure 32:** Waterborne Interior wall paint and our samples universal colorants (rub-out test).

**Table 16:** Results of CIE-lab measurements of the samples from Figure 32.

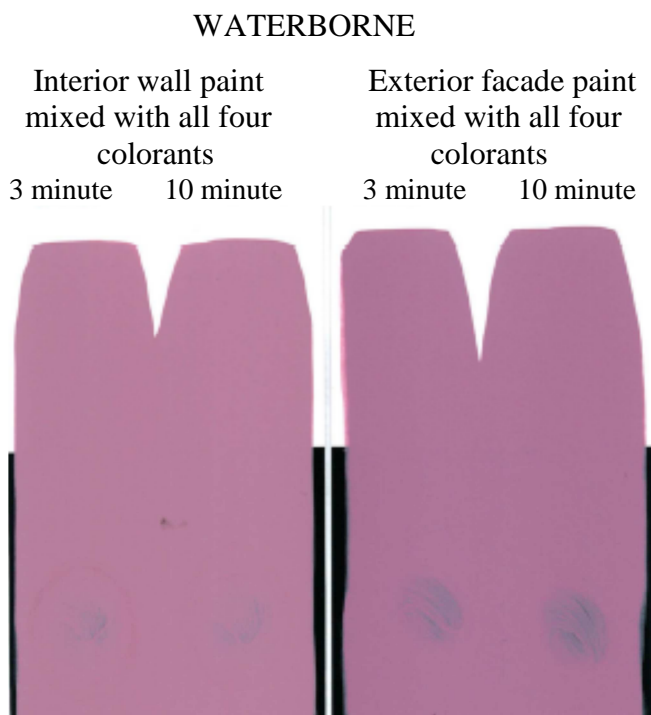
CIE L*a*b* Colour Difference for Interior wall paint with colorants difference in rub out circle								
Colorants	DL*	Da*	Db*	DC*	DH*	DE*	CMC-DE	C. strength
ORANGE	-0.19	0.17	0.51	0.41	0.35	0.58	0.38	103.21 %
RED OXIDE	-0.22	0.19	0.32	0.29	0.23	0.43	0.33	102.20 %
VIOLET	-0.58	0.40	-0.13	0.30	0.29	0.71	0.56	103.97 %
MAGENTA	-0.58	1.05	-0.20	1.04	0.23	1.22	0.66	105.54 %

The rub-out test provides information on the compatibility of the base and the colorant. The results of this test where the spot of a rub-out is measured are less good. In this case we used the surface around the circle (rub-out) as the standard. The measured surfaces which show the results in Table 16 are the circles (rub-out). It is evident for all the samples that the colour strength has risen from 2.20 – 5.54 %. As long as the colour strength is in the area of 95 – 105 % and DE is less than 1, there is no need to make any optimization of the tested products. But if a colour strength is above or below those values optimization of the products is necessary. When DE is in question, than we also have to check CMC-DE since normally the value of CMC-DE is lower than that of DE. CMC-DE represents the difference which the human eye can notice. DE represents the difference which an instrument can measure. From

our measurements we can say that we have good results with three colorants: orange, red oxide and violet. Less favourable results were obtained with the magenta colorant. At this stage it is difficult to conclude where optimization is needed (on base or colorant or both) in order to reach a good compatibility.

Results of all the four colorants (with higher colour strength) point out that more colour strength from the colorant can still be attained, since with the rub-out test we are creating a higher pressure on the base and the colorant to be mixed. However some differences in measurements are also possible because of the different surfaces and thicknesses of the measured samples and it is therefore logical that we cannot expect 100 % good result.

We put all four colorants in one base: 1% of each colorant to check compatibility between the colorants and the system. Compatibility and wetting test also show good results with both bases with all four colorants (violet, magenta, red oxide and orange colorant - Figure 33).



**Figure 33:** Colour shades on waterborne products, wetting and compatibility.



**Table 17:** Results of CIE-lab measurements of the samples from Figure 33.

CIE L*a*b* Colour Difference with all four colorants, difference in rub out circle								
Sample	DL*	Da*	Db*	DC*	DH*	DE*	CMC-DE	C. strength
Interior	-0.02	0.21	-0.08	0.22	-0.05	0.22	0.14	100.06 %
Exterior	-0.05	0.02	-0.02	0.03	-0.01	0.06	0.05	100.35 %

Figure 33 shows good compatibility and wetting results of the colorants in the waterborne bases: B1 – exterior façade paint and in B1 – interior wall paint. Results from Figure 35 are also confirmed in Table 17 where there is almost no difference in the colour strength of both bases.

### 4.3. Colorant in solventborne products

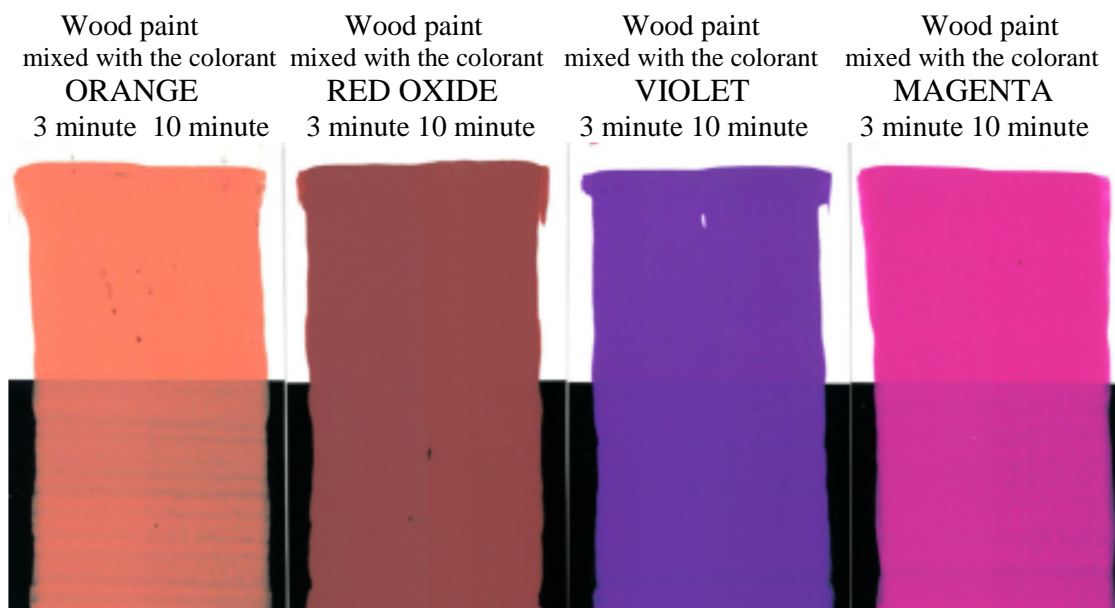
We tested colorants in two solventborne paints: paint for wood and paint for metal. We carried out the same tests as with waterborne paints (wetting test, compatibility test and test with more than one colorant).

Wood paint only has one base B3 (0 % of TiO<sub>2</sub> – white pigment). Paint for metal (enamel) has 3 B bases: B1, B2 and B3. B1 has 20 % of TiO<sub>2</sub> (white pigment), B2 has 9 % of TiO<sub>2</sub> (white pigment) and B3 has 0 % of TiO<sub>2</sub> (white pigment).

The volume of the colorants is on average the same for waterborne paints as it is for solventborne paints. Averagely 3 % of colorants are added to B1, 8 % to B2 and 10 % to B3.

For this thesis we tested the colorants with solventborne products only in B3. Samples were prepared differently as for B1. Since B3 is without any pigment we had to add a white colorant to make the wetting and compatibility results clearer. If we had added only one of our testing colorants we could not have seen any possible problems with compatibility since B3 base is transparent. We added 8 % of solventborne white colorant together with 4 % of our testing colorant.

Wetting tests with VIOLET, MAGENTA and ORANGE colorants were good. None of the two bases demonstrated any differences in their colour strength during 3 to 10-minute shaking (Figure 34). However there is a difference with the red oxide colorant sample. The sample has a wetting problem with this base.



**Figure 34:** Solventborne wood paint and our samples universal colorants (wetting test 3 and 10 minutes).

**Table 18:** Results of CIE-lab measurements of the samples from Figure 34.

CIE L*a*b* Colour Difference for solventborne wood paint with colorants								
Colorants	DL*	Da*	Db*	DC*	DH*	DE*	CMC-DE	C. strength
ORANGE	0.24	0.15	0.22	0.25	0.08	0.36	0.22	99.25 %
RED OXIDE	-0.41	1.15	1.36	1.60	0.78	1.83	1.20	106.06 %
VIOLET	-0.09	0.10	0.11	-0.05	0.14	0.17	0.13	100.57 %
MAGENTA	-0.18	0.62	0.33	0.51	0.48	0.73	0.40	102.57 %

As can be seen in Figure 34 the red oxide colorant shows wetting problems. This is also measured with an instrument - results can be seen in Table 18.



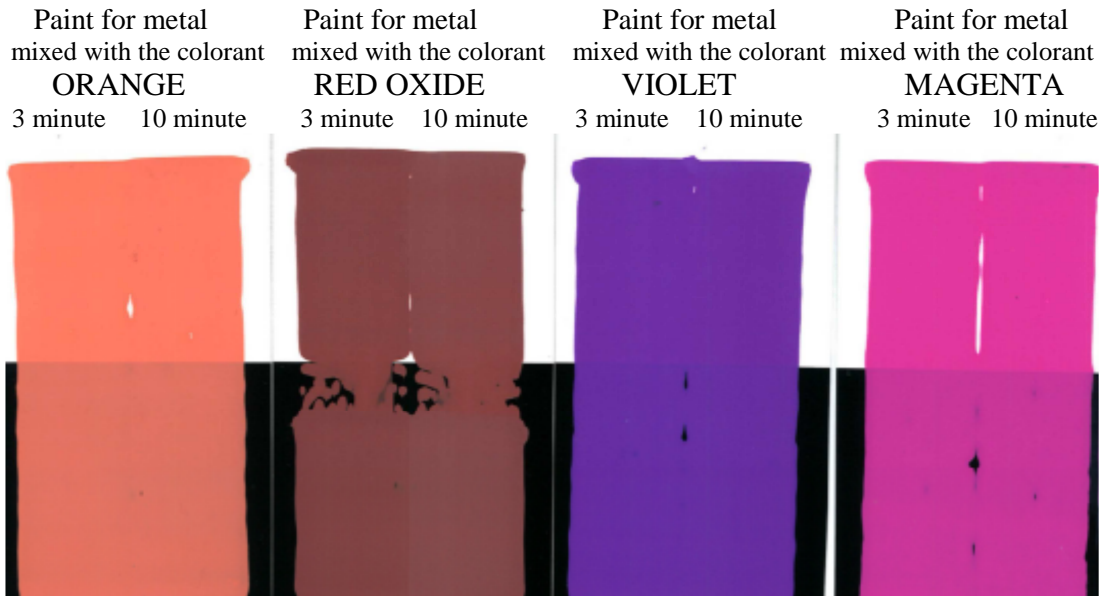
**Figure 35:** Solventborne wood paint and our samples universal colorants (rub-out test).

**Table 19:** Results of CIE-lab measurements of the samples from Figure 35.

CIE L*a*b* Colour Difference for wood paint with colorants, difference in rub out circle								
Colorants	DL*	Da*	Db*	DC*	DH*	DE*	CMC-DE	C. strength
ORANGE	0.16	0.03	0.39	0.25	0.3	0.42	0.29	100.03 %
RED OXIDE	0.45	0.33	0.44	0.45	0.3	0.71	0.56	97.96 %
VIOLET	-0.47	0.68	-0.41	0.68	0.42	0.93	0.62	103.37 %
MAGENTA	-0.32	1.15	0.32	0.98	0.69	1.24	0.62	104.25 %

Results (Figure 35 and Table 19) show good compatibility in the solventborne wood paint.

Like in the wood paint the red oxide colorant shows some wetting problems in the metal paint as well.



**Figure 36:** Solventborne paint for metal (enamel) and our samples universal colorants (wetting test 3 and 10 minutes).

**Table 20:** Results of CIE-lab measurements of the samples from Figure 36.

CIE L*a*b* Colour Difference for solventborne metal paint with colorants								
Colorants	DL*	Da*	Db*	DC*	DH*	DE*	CMC-DE	C. strength
ORANGE	0.20	0.03	-0.08	-0.03	-0.08	0.22	0.17	98.51 %
RED OXIDE	0.62	-0.48	-0.39	-0.59	-0.20	0.88	0.7	95.05 %
VIOLET	-0.07	0.05	0.07	-0.03	0.08	0.11	0.09	100.46 %
MAGENTA	-0.06	-0.06	0.02	-0.06	0.00	0.09	0.06	100.48 %

Normally when a colour strength is lower than 100 % for a sample shaken longer than 10 minutes there are less logical explanations. But in our case we can explain this with the fact that a white colorant was in use as well. We used a white colorant together with the testing colorant, because B3 which were used for testing in solventborne paints, are transparent. The transparency of B3 bases would not show any results when there is a question of compatibility (rub-out test). All the results would show good compatibility even if compatibility would not be necessarily good. The use of a white colorant was therefore logical. So when the colour strength, in our case for the red oxide colorant, was 95.05 % (less than 100 %) it means that in the first 3 minutes the red oxide colorant dominates over the white colorant. After 10 minutes of shaking, the white pigment is mixed better with the red oxide colorant and

the base. Therefore we cannot conclude that the wetting of red oxide colorant is bad. What we can conclude is that the red oxide colorant shows different behaviour when it is mixed together with a white colorant. It is apparent from Table 20 that VIOLET and MAGENTA colorants are wetted in optimum way.

The presumption that all the four colorants are in the acceptable deviation still holds true.

We did rub out test on our samples (Figure 37).



**Figure 37:** Solventborne paint for metal (enamel) and our samples universal colorants (compatibility test, rub-out test).

**Table 21:** Results of CIE-lab measurements of the samples from Figure 37.

CIE L*a*b* Colour Difference for metal paint with colorants, difference in rub out circle								
Colorants	DL*	Da*	Db*	DC*	DH*	DE*	CMC-DE	C. strength
ORANGE	0.50	-0.10	-0.84	-0.58	-0.61	0.98	0.68	94.48 %
RED OXIDE	0.78	4.40	4.67	5.85	2.63	6.46	4.25	105.63 %
VIOLET	0.73	0.23	-0.33	0.40	0.04	0.83	0.71	95.19 %
MAGENTA	0.04	0.10	-0.11	0.13	-0.07	0.15	0.07	99.81 %

Table 21 shows colour differences between circle (rob-out) and the rest of the surface and proves the statements predicting the result in the wetting test. The red oxide colorant certainly has a compatibility problem that needs improvement. The result

DE points to this because it is much bigger than 1. All the other colorants have DE of less than 1 and the colour strength is in accepted values.



**Figure 38:** Colour shade on solventborne products; wetting and compatibility test.

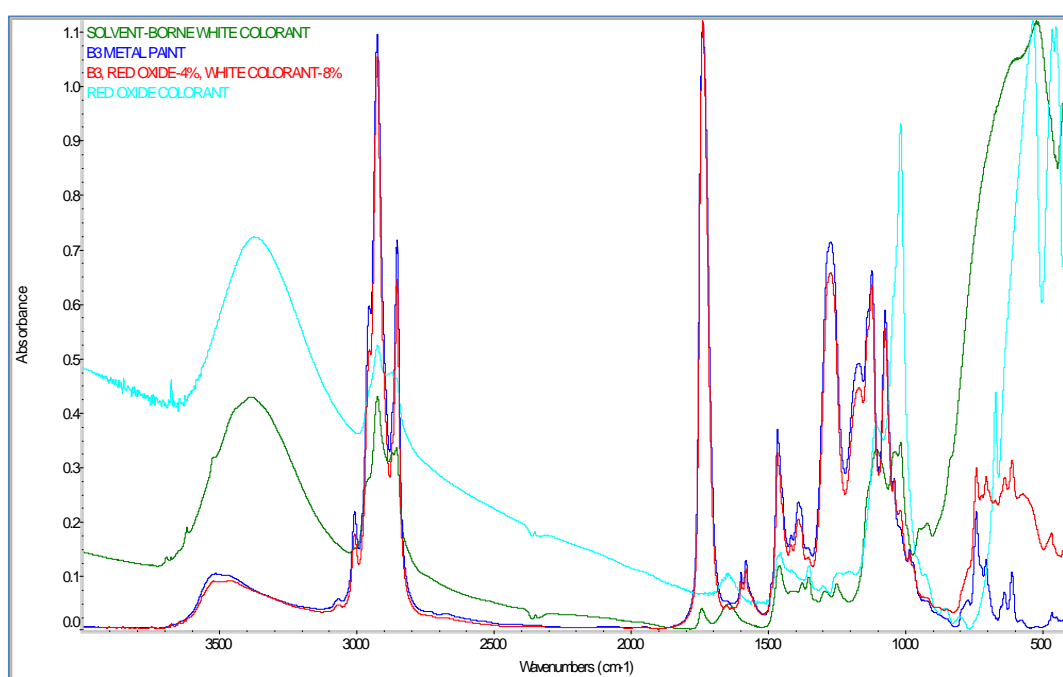
**Table 22:** Results of CIE-lab measurements of the samples from Figure 38.

CIE L*a*b* Colour Difference with all four colorants, difference in rub out circle								
Sample	DL*	Da*	Db*	DC*	DH*	DE*	CMC-DE	C. strength
Metal	0.08	0.17	-0.04	0.17	-0.02	0.19	0.13	99.45 %
Wood	-0.28	0.13	-0.30	0.15	-0.29	0.43	0.36	101.43 %

Results of measured values in Table 22 show no compatibility or wetting problem when all four colorants (RED OXIDE, ORANGE, VIOLET and MAGENTA) are used to form a colour shade in solventborne wood or metal paint. This statement holds true only when the percentage of each colorant is not higher than one.

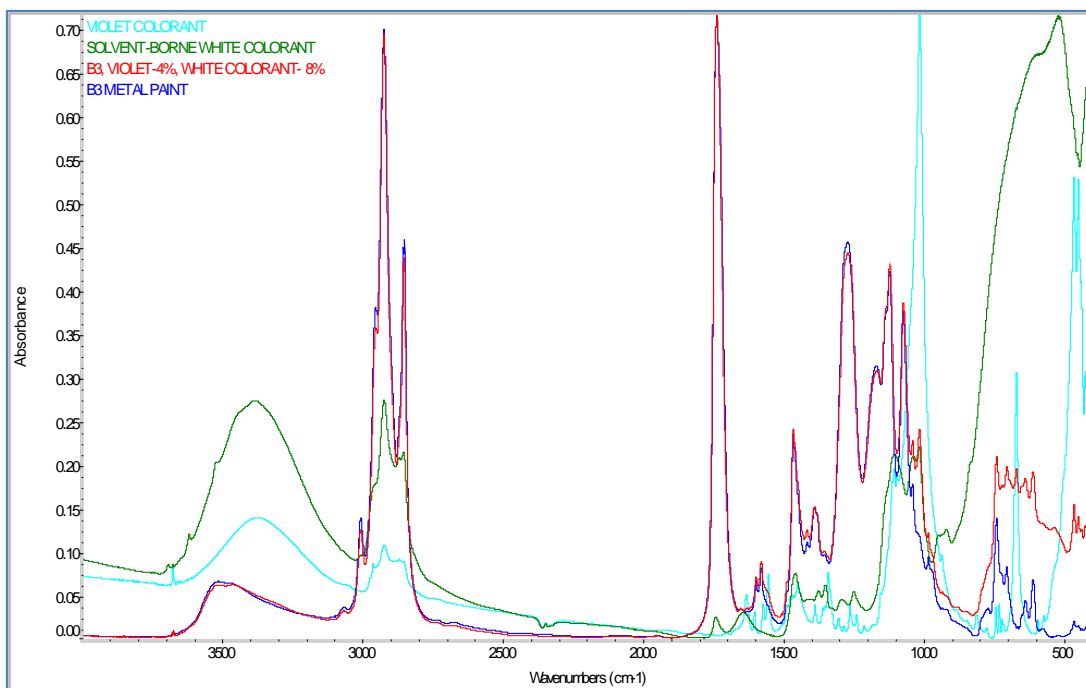
#### 4.4. Analytical testing of violet and red oxide colorant with FTIR spectroscopy

One of the final tests to support our work, the test with which we could confirm or deny our success in producing universal colorants, examined the colorants in different systems (waterborne and solventborne). We examined chemical stability. We performed those tests with the violet colorant (organic pigment) and with red oxide colorant (inorganic pigment).



**Graph 40:** FTIR spectra of the samples: red oxide colorant, solventborne white colorant, B3 Metal paint and mixture of B3, red oxide colorant and solventborne white colorant.

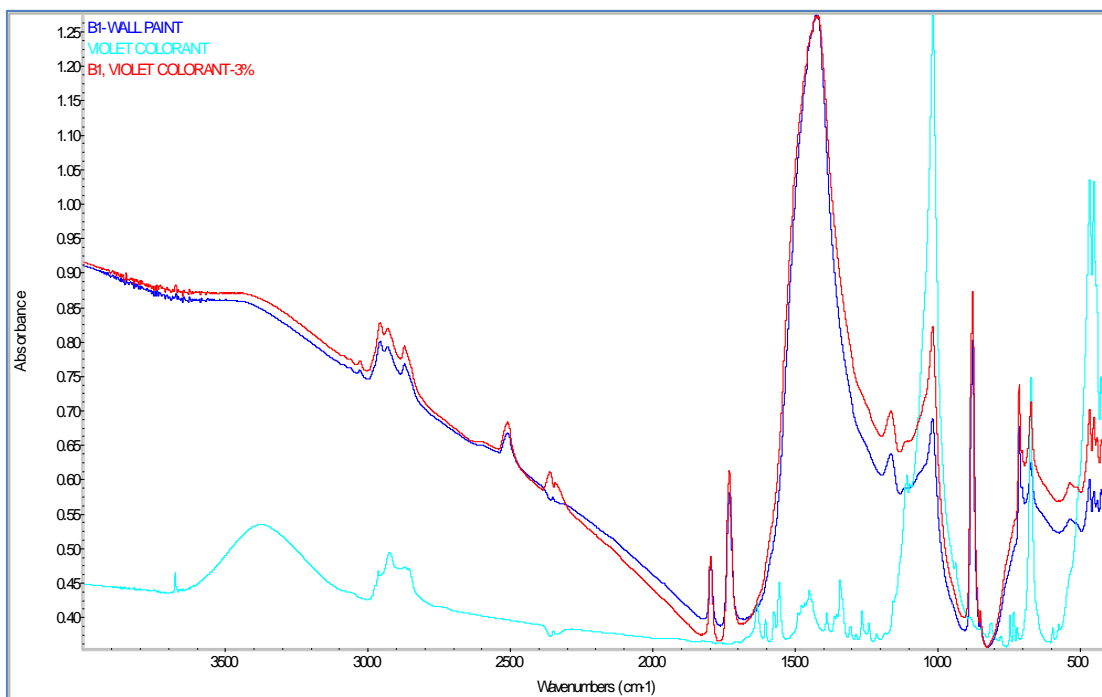
The red oxide colorant is seen in Graph 40 and is marked in the turquoise line; the solventborne white colorant in the green line. The B3 metal base is marked in the blue line. The red line shows the mixed material consisting of the base and the colorants. When interpreting the spectra from Figure 40 it should be stated that the red line represents 88 wt.% of the B3 metal base, 8 wt.% of the white colorant and 4 wt.% of the red oxide colorant. From IR spectra of (mixture of B3, red oxide colorant and solventborne white colorant) we can note there is no chemical reaction between any of the three different media.



**Graph 41:** FTIR spectra of the samples: violet colorant, solventborne white colorant, B3 Metal paint and a mixture of B3, violet colorant and white colorant.

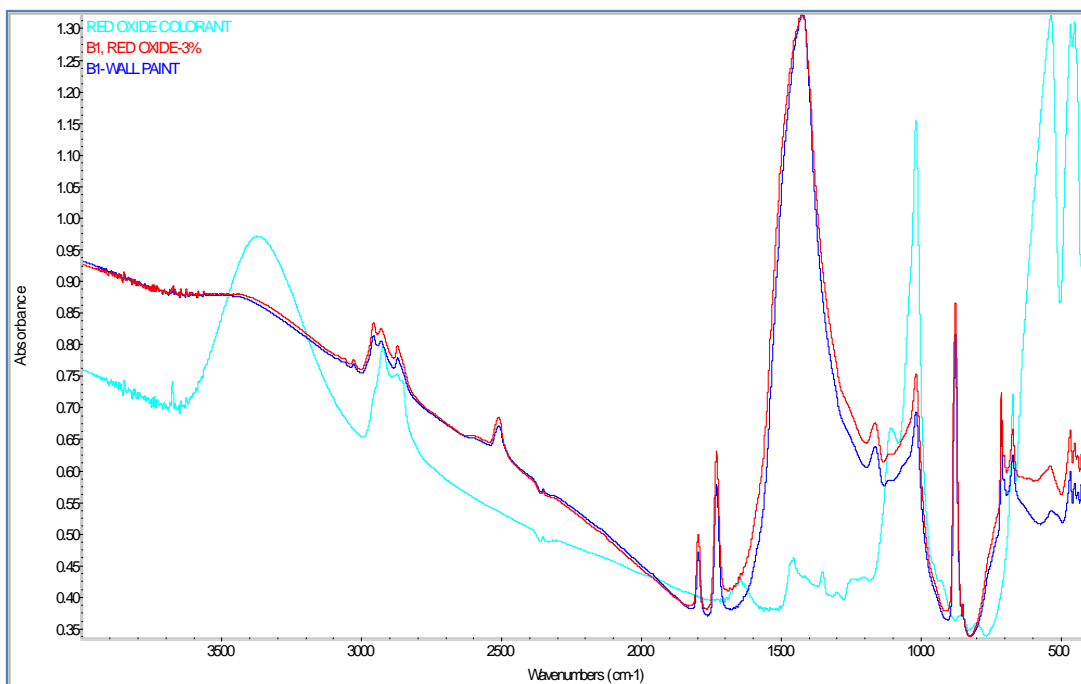
In Graph 41 we present the following spectra: the violet colorant is marked in turquoise line, solventborne white colorant in the green line, B3-metal base in blue line. The red line represents the mixed material consisting of the base and the colorants. By interpreting the spectra from Graph 41 it should be stated that the red line represents 88 wt.% of the B3 metal base, 8 wt.% of the white colorant and 4 wt.% of the violet colorant. From IR spectra (mixture of B3, violet colorant and solventborne white colorant) we can see no chemical reaction between any of the three different media.





**Graph 42:** FTIR spectra of the samples: violet colorant, B1 wall paint and a mixture of B1 and violet colorant.

In Graph 42 we present with the following: the violet colorant is marked in the turquoise line, the B1 base wall paint in the blue line and the mixture of the base and the colorants in the red one. When interpreting the spectra from Graph 42 it has to be made known that the red line represents 97 wt.% of the B1 wall paint and 3 wt.% of the violet colorant. From IR spectra (mixture of B1, and violet colorant) we can state that there is no chemical reaction between the two different media.



**Graph 43:** FTIR spectra of the samples: red oxide colorant, B1 wall paint and mix of B1 and red oxide colorant.

In Graph 43 we present with the following: the red oxide colorant is marked in turquoise line, the B1 base wall paint in blue line, and the red line represents the mixture of the base and the colorants. By interpreting the spectra from Graph 43 it must be made clear that the red line represents 97 wt.% of the B1 wall paint and 3 wt.% of the red oxide colorant. From FTIR spectra (mixture of B1, and red oxide colorant) we can see that there is no chemical reaction between any of the two different media.

FTIR spectra were made 4 days after mixing at normal conditions. The main reason for employing this method was to support the compatibility and wetting tests, whose results had suggested that preparation of universal colorants was successful. FTIR spectra of the mixed materials show no chemical reactions among the different components. It is seen from each spectra that there is no new peak and that not one peak has disappeared. All peaks are from the materials which were mixed together.

From this we can conclude that only a physical reaction was observed since the spectra show a normal deviation which is due to the different percentages of the materials. The same was observed in waterborne and solventborne paints. Having said this we can conclude that this method also proves we have indeed produced universal colorants.

## 4.5. Colorants in dispensing machine

To avoid possible unfavourable cases in the market we also tested the colorants in the dispenser - where colorants will generally be in use. The results can be seen from the tables below.

**Table 23:** Drying test on the nozzle.

Testing colorants on the dispenser below pump technology					
Test	Period of test	Sample			
		Violet V-8A	Magenta V-6	Red oxide V-6A	Orange V-10
Drying test on the nozzles	Sponge wetted every day (checking 7 days)	No drying problem on the nozzle	No drying problem on the nozzle	No drying problem on the nozzle	No drying problem on the nozzle
	Sponge wetted every week (checking 3 weeks)	No drying problem on the nozzle	No drying problem on the nozzle	No drying problem on the nozzle	No drying problem on the nozzle
	Sponge checked every two weeks (checking 3 times)	No drying problem on the nozzle	No drying problem on the nozzle	When dispensed colorant was not falling in horizontal direction	No drying problem on the nozzle
	Sponge checked every month (checking 2 times)	No drying problem on the nozzle	When dispensed colorant was not falling in horizontal direction	Pump of dispenser need it more power to dispense. Drying problem.	When dispensed colorant was not falling in horizontal direction

Drying test on the nozzles was necessary to test the most sensitive part of a dispenser. Nozzle part is situated in the middle of a dispenser (on front). We find this

part the most important because at this point colorants are dispensed into the base can. On this type of a dispenser all 16 canisters have nozzles in the same area in the circle of diameter which measures 5 cm. Every nozzle has a diameter of 8 mm. For all the nozzles there is one sponge, which is wetted and takes care that nozzles are in the humidity area. Problems appear when a colorant dries on the nozzle and that normally happens for this type of a dispenser when the sponge is without any water.

“Sponge wetted every day” means that we took out the sponge and wetted it every 24 hours. At the same time we dispensed 3 ml of each colorant. At dispensing we did not notice any change. All the colorants were dispensed horizontally. No drying was noticed. The tests lasted for 7 days.

“Sponge wetted every week” means that we took out the sponge and wetted it every 7 days. At the same time we dispensed 3 ml of each colorant. At dispensing we did not notice any change. All the colorants were dispensed horizontally. No drying was noticed. The tests lasted for 3 weeks.

“Sponge wetted every two weeks” means that we took out the sponge and wetted it every 14 days. At the same time we dispensed 3 ml of each colorant. At dispensing we did not notice any change with colorants Violet V-8A, Magenta V-6, and Orange V-10. Colorants were dispensed horizontally. No drying was noticed. A difference was noticed with the Red oxide V-6A colorant - the colorant showed its first drying problems with non-horizontal dispensing. What happened was that the sponge could not give the same humidity concentration after 14 days as it could after 7 days. And for the Red oxide V-6A sample this already meant the first drying problems. Although it has to be added that this first drying identification is not a problematic one.

“Sponge wetted every month” means that we took out the sponge and wetted it every 30 days. At the same time we dispensed 3 ml of each colorant. At dispensing we did not notice any change with the Violet V-8A colorant. A difference was noticed with the following colorants: Magenta V-6, and Orange V-10, where the colorants showed their first drying problems through non-horizontal dispensing. What happened was that the sponge could not give the same humidity concentration after 1 month as it could after 14 days. And for some samples (Magenta V-6, and Orange V-10) this already meant the first drying problems. For the Red oxide V-6A sample this already meant a too long time period in which the sponge was not wetted. The pump in the

canister of the Red oxide V-6A colorant had problems coming out (which means that the colorant was dried) which prevented the colorant to dispense without a problem. From this test we could conclude that a sponge must be checked and wetted every week in order to prevent drying of the colorant on the nozzle.

**Table 24:** Condition of the colorants in the canister.

Testing colorants on the dispenser below pump technology					
Test	Period of test	Sample			
		Violet V-8A	Magenta V-6	Red oxide V-6A	Orange V-10
Condition in the canister	1 week	No change notice	No change notice	No change notice	No change notice
	3 weeks	No change notice	No change notice	No change notice	No change notice
	2 months	No change notice	thixotropic part of colorant on the stirrer part	No change notice	No change notice
	3 months	No change notice	thixotropic part of colorant on the stirrer part	No change notice	thixotropic part of colorant on the stirrer part

Checking colorants in the canister is a test very much connected to the rheology of colorants. Canisters in which we tested our colorants had a volume of 2.5 litres. Of course dispensers can have a canister with a different volume (this can be from 1.5 litres to 5 litres and more). The volume depends on the sector where the dispenser will be in use (decorative, industrial or automotive). We filled up each canister with 2 litres of colorant.

We did this test because we knew that colorants generally had problems with increasing viscosity occurring over time at high shear stress. Viscosity can increase in a shorter time when a colorant is exposed to stirring forces. This is the case when a colorant is in a canister. Every canister has the option to stir colorants. Stirrer in the canisters is used to prevent sedimentation of the colorant. Stirring is set using a program. 16 canisters dispenser offers the option to set the same stirring for every

canister. That is not an optimal option since every colorant has specific characteristic and therefore a different optimal stirring time. For our test we stir every hour for five minutes. The problem with stirring is that the rheological structure is destroyed by any stirring and when stirring stops the rheological structure again forms back. The structure is never the same, with every stirring viscosity rises and this also happens since over time the solvent-water goes out of the system. As we could also see in rheological graphs where the flow curves are presented, thixotropic behaviour also increases over time.

From Table 24 we see the results and a difference were noticed on the magenta V-6 and orange V-10 samples. It is evident that the stirrer needs more power to stir. Moreover in the middle of the canister there were very thick sectors of colorants with higher viscosity. This change on colorants happens when the same batch of a colorant is in a canister for a long period of time (2 to 3 months) and when stirring is intensive (every hour for 30 seconds).

Taking into account our results and the fact that our samples did not show any sedimentation problems during the research, we conclude that stirring of our product can be set on every three hours for 30 seconds.

**Table 25:** Weighing colorants on different period.

Testing colorants on the dispenser below pump technology					
Test	Period of test	Sample			
		Violet V-8A	Magenta V-6	Red oxide V-6A	Orange V-10
Weighing after one week	1 ml	0.99 ml	1.02 ml	1.00 ml	0.97 ml
	10 ml	10.00 ml	10.24 ml	10.10 ml	9.89 ml
	100 ml	101.50 ml	102.07 ml	100.30 ml	99.03 ml
Weighing after three weeks	1 ml	1.03 ml	1.01 ml	1.03 ml	0.98 ml
	10 ml	10.20 ml	10.33 ml	10.16 ml	9.87 ml
	100 ml	100.50 ml	101.72 ml	100.14 ml	99.33 ml
Weighing after three month	1 ml	0.98 ml	1.06 ml	0.98 ml	0.96 ml
	10 ml	10.10 ml	10.14 ml	10.26 ml	9.79 ml
	100 ml	101.32 ml	101.78 ml	100.73 ml	98.91 ml

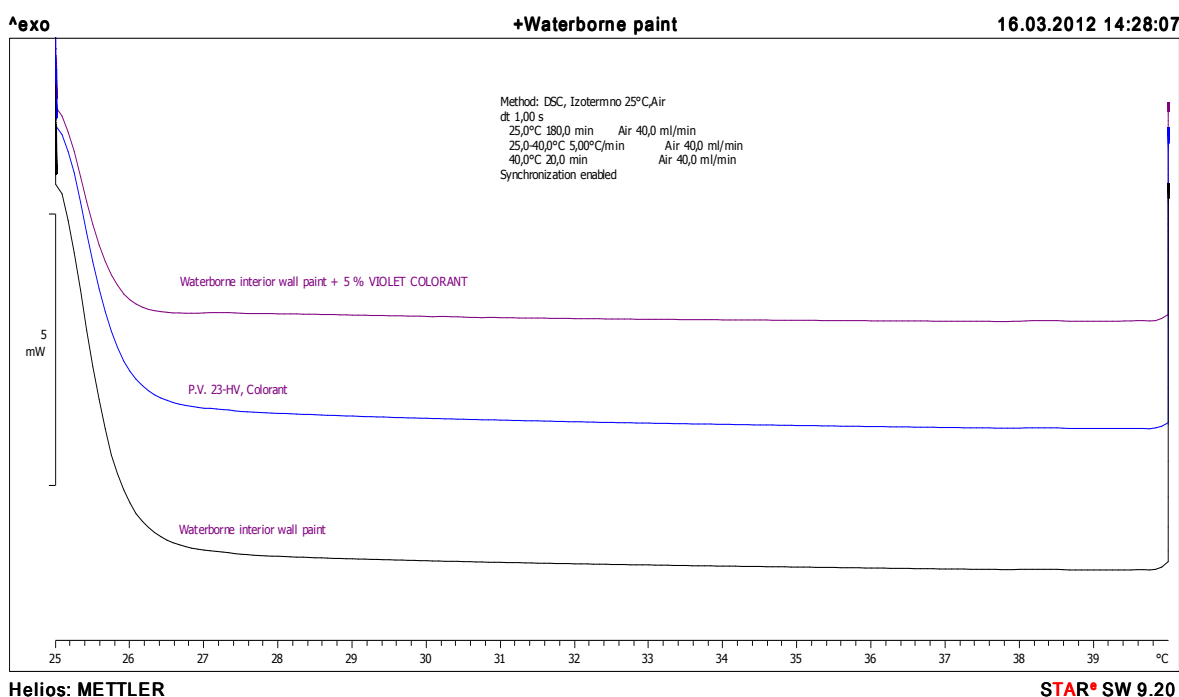
Weighing colorants in different time periods is one logical test which provides important results about the stability of a colorant in a dispenser. Of course such results also depend on the quality of the dispenser. Since we have experience with below pump technology dispenser we know that it can be used for that kind of a test. Results in Table 25 are in millilitres. We normally measured the results with a scale and calculated them with the density. In mix system we have a gravimetric and volumetric dispensing; in our case we have volumetric. This is why it is important for us that the machine dispenses the right volume (recipes for colour shades are made in volumes). The test lasted over 3 months. First we did the calibration of the dispenser. For this type of a dispenser which has below pump technology calibration is required. With the help of calibration a dispenser gets the information about how much the pump has to be moved to dispense a certain amount of colorant.

Before we did the weighing of a certain amount, we had dispensed 20 ml to avoid possible mistakes (if a colorant is too long in a tube there can be some water evaporation that can affect the results). This purge before testing was performed since with this test we wanted to determine the stability of a colorant in the canister and not in the first centimetres of the tube.

In Table 25 we can see that the results are in the acceptable range since the producer of dispenser also applies in their technical data sheet a possible deviation of  $\pm 1$  %. Our results show in some cases also the deviation of more than 2 % but not more than 3 %, which is still in the area where mistake on colour shades cannot be noticed by the human eye. It depends on the recipe of the colour shade because the human eye can see small differences on blue shades more easily than on the other colours of shades.

## 4.6. Differential scanning calorimetry

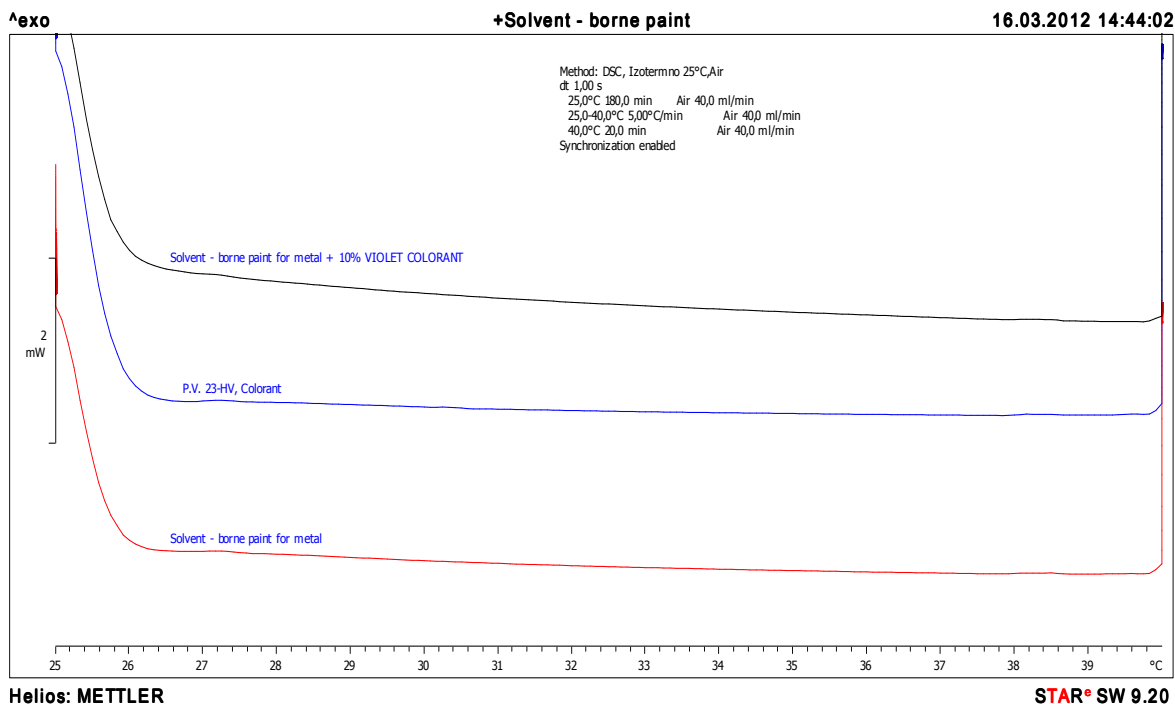
The DSC measurement was performed in order to see if there is any chemical reaction between the colorants and the base paints. We also employed the FTIR spectroscopy to check for possible chemical reactions. But since the DSC measurement is more precise in this aspect we decided to check our samples also with this method.



**Graph 44:** Waterborne base and violet colorant.

In Graph 44 we have a measurement of the waterborne interior wall paint, which is represented by a black line at the bottom. The Violet colorant is marked in the blue line in the middle and the mixture consisting of 5 % of violet colorant and waterborne interior wall paint is marked in magenta line at the top. From this measurement we can say that there is no chemical reaction between the waterborne interior wall and violet colorant. There is no peak up-exothermic (which would mean an exothermic reaction in our samples) and there is no peak down-endothermic (which would mean an endothermic reaction in our samples).





**Graph 45:** *Solventborne base and violet colorant.*

In Graph 45 we have a measurement of solventborne paint for metal, which is represented in the red line at the bottom. The violet colorant is shown in a blue line in the middle and the mixture consisting of 10 % of violet colorant and the solventborne paint for metal is marked in the black line at the top. From this measurement we can say that there is no chemical reaction between the solventborne paint for metal and the violet colorant. There is no peak up-exothermic which would mean an exothermic reaction in our samples. There is no peak down-endothermic which would mean an endothermic reaction in our samples.

These measurements also inform us that our samples are stable at temperature in the range from 25°C to 40°C.

#### **4.7. Universal colorants – VOC measurement**

VOC values have been measured in all four colorants and the measurements have indicated some VOC content in all four colorants.

Universal violet colorant VOC content was 0.70 % by mass. One litre of colorant with density of 1.35 kg/l had 9.5 g of VOC content (calculated using Equation 1).

Since VOC value is more important on 1 litre of a “ready-to-use” product, VOC should be calculated for each colour shade. If we add 5.0 % of the Violet colorant on volume that we input in the product the maximum amount of VOC content is 0.47 g.

Universal red oxide colorant had 5.4 g of VOC content per one litre of colorant.

Universal orange colorant had 8.9 g of VOC content per one litre of colorant.

Universal magenta colorant had 4.4 g of VOC content per one litre of colorant.

At this point we went looking back in order to determine which raw material could have affected VOC content. It is true that from the technical data sheet we did not notice whether all the raw materials used are VOC-free, but at the same time there was no information about any VOC content in any of them. Of course we could notice from some technical data that there is a possibility of some VOC content in the raw materials. But since the producer did not add this information in the technical data sheet, we could not know the percentage of VOC and it needed consideration. However VOC content of less than 1.0 % per litre exists and will not affect the “ready to use” base product, because the lowest VOC content in decorative coatings is 30 g/litre. By adding our colorants to the base paint whose VOC content is 30 g/litre we decrease the VOC content of that paint per litre. Of course our goal in the future will be to find the exact raw material (in our formulations) with VOC content and try to make colorants without that raw material.

## 5. Discussion

Our intention was to prepare colorants which could be used in both systems: waterborne and solventborne. When choosing raw materials we were looking for such that, according to producers, can be used in both systems. It was not until we got the last results that we could be sure if we in fact had colorants justifying our intention.

Many factors were to be considered during the preparation of the colorants. We had to keep in mind that producing a colorant in a production plant causes much more deviation than in a laboratory. Because of that recipes should be prepared in a way that makes corrections as simple as possible.

A solvent and a binder are two basic raw materials which can be used to achieve the required results when corrections on the batches are needed. In our case with colorants, where we had no binders only water as a solvent in our recipes, we had to prepare an additional product to function as a binder. Both of the mentioned raw materials (water and binder) are necessary to be able to get the sought coloristic and rheological parameters.

If we used only water for making corrections on coloristic and rheological parameters of our universal colorants in the production plant we would not be successful. We would be able to correct coloristic parameters but not rheological. The same holds true for the rheological parameters: in some cases we would be able to correct rheological but not coloristic parameters. Normally all the products produced in a production plant are prepared in such a way that coloristic results are always better than needed which means that colour strength is higher than 100 %. By adding solvent, water, binder or other raw materials which we use to correct rheological parameters we always affect also the coloristic parameters (colour strength). That is why it is important that we produce a product whose colour strength after rubbing is high enough that it allows us to make the required corrections by inputting other raw materials.

Because we cannot use binders to correct coloristic and rheological parameters in our universal colorants we prepared a filler paste with rheological parameters similar to those of colorants. By preparing a filler paste with similar rheological parameters as we usually expect from the colorants we could regulate the coloristic of that colorant without changing rheological parameters of the product.

At first we had to prepare stable colorants, which means we had to test them in different conditions. When a colorant stays stable even after having been exposed to temperature of 40°C for one month we conclude that it is a stable pigment concentrate (colorant). This stabilisation was checked with rheological flow tests.

#### Filler paste

We did eleven rubbed versions in a laboratory and one in a production plant. For the purpose of this work the last six versions in the laboratory, where we used finntalc, are important. As mentioned, finntalc was chosen because it gives acceptable results. However, its effect on the gloss of the final paint is greater (due to bigger particles present in finntalc). Since the addition of the colorant into the base paint is not higher than 10%, we did not add more than 4% of finntalc in the final colour formulations and this did not affect the gloss in any critical way. Another important reason lies in the price: the price of microtalc is 240 % higher than the price of finntalc.

At stabilisation of the filler paste we were looking for a formulation whose viscosity at low shear stress would be under  $10^2$  Pas and at high shear stress between 0.1 and 1 Pas. This was achieved by using dispersing agent 2. We saw that the trend of viscosity at low shear stress (Graph 4) drops by increasing the volume of dispersing agent 2. Aging the version from the production plant in a stove at 40°C confirmed that we succeeded in preparing a stable filler paste.

#### Violet colorant

We did ten rubbed versions in a laboratory and one in a production plant. After the first three versions we started using a stabilized filler paste. We saw that using a filler paste in a rubbing paste together with a pigment is better from the point of view of stabilisation. What we could assume is that a filler paste is more attached into the system if it is rubbed together with other raw materials. After we optimised the rubbing recipe we tested the behaviour of the samples when water or filler paste is added at the end. Adding water and a filler paste at the end is important from the point of view of production - when certain coloristic properties of a colorant has to be achieved. Violet colorant was prepared in a production plant without any problems.

#### Magenta colorant

We made eight rubbed versions in a laboratory. After the first four versions we started using a confirmed filler paste. At first we had some problems with the

thickening of the samples. With the last version we used two new raw materials: wetting and dispersing agent 3 and dispersing agent 4. Graph 21 shows that the flow curve moved up and did not change the shape when we used wetting and dispersing agent 3 and dispersing agent 4. On the contrary, where we used wetting and dispersing agent 1 the flow curve moved up and also changed the shape as can be seen in Graph 20. Better stabilisation is therefore logical in V-6 sample. We can say that the stabilisation was not perfect but it was acceptable since the colorant was flowing without any problems, even when the sample was stirred with a stick after aging.

#### Red oxide colorant

We did seven rubbed versions in a laboratory. After the first four versions we started with the use of a confirmed filler paste. We already confirmed V-4 as an acceptable sample. Therefore our goal was to prepare the same sample with a new filler paste. With version V-6 (A and B) we managed to prepare a stable colorant also after aging in a stove at 40°C. Like with other colorants, after rubbing we added different volumes of water and filler paste in order to see the stabilisation of the colorant, since this option (of adding water or filler paste) is possible in a production plant.

#### Orange colorant

We did twelve rubbed versions in a laboratory. After the first two versions we started using a confirmed filler paste. It was not possible to attain the required rheological properties with wetting and dispersing agent 1. When making the samples with dispersing agent 3 we achieved the required rheological behaviour also after aging the samples in the stove. At the end we had two versions with dispersing agent 3 which were acceptable in terms of quality. It would be impossible to conclude which of the two samples is better just on the basis of hand stirring; this decision was reached after rheological measurements. Conclusions based on those measurements are in favour of the sample with less filler paste and more water (Graph 39).

Rheological tests in this piece of academic work are used to show physical stability of our samples. We were satisfied with the reached physical stabilisation. However, we can say from the rheological measurements that physical stabilisation is dropping in this order: filler paste, red oxide colorant, violet colorant, orange colorant and magenta colorant. It can be concluded that physical stabilisation of a colorant is reached more easily with inorganic pigments. This is the experience we got because

we had less different versions with inorganic (filler, red oxide) and the first versions were not so bad either. What is interesting with violet is that it was prepared with approximately 40% of clear filler in the recipe and only 8% of the violet pigment.

That is why we also think that the violet colorant was more stable; it had much more inorganic particles which had to be stabilised in the system. Nevertheless stabilisation of all the four colorants was reached on the level which allowed us to move forward with our tests.

Next testing stage was testing the compatibility of our colorants with waterborne and solventborne paints (products). Results in this section confirmed that we have universal colorants since compatibility problem was only noticed with red oxide colorant when it was added alone in bases for wood and metal. We did not pay much attention to that because when the same colorant was added together with other colorants in the same solventborne bases the compatibility problem was no longer noticeable.

After we got a confirmation that our colorants are stable with our rheological measurements (flow test) and that they are universal (for waterborne and solventborne systems) we decided to test them in a dispenser machine. Test in a dispenser machine is very logical because colorants before being sold to the final users can spend from 0 up to 3 month in canisters. Of course the time in a dispensing machine depends on the use of a certain colorant. Results of testing on the dispensers were equal to rheological tests in the way that we also saw good stability of the red oxide and violet colorant and the start of pseudoplastic behaviour on the orange and magenta colorant.

DSC and FTIR measurements are two methods which were employed to see the chemical stabilisation. It was confirmed with both of them that our colorants are stable.

FTIR spectroscopy was used to check two colorants (red oxide and violet colorant) in both systems (waterborne and solventborne). DSC differential scanning calorimetry was used to check the violet colorant in both systems.

Violet and oxide red colorant were chosen in order to confirm the chemical stability of the system. One colorant with an organic pigment and one with an inorganic pigment was selected. Since there was no significant change in any of the four colorants, we assumed them to be chemically stable. We wanted to check and

confirm this with FTIR and DSC measurements. So we chose violet colorant to check the chemical stability because colorant has the biggest volume of the filler paste. We assumed that if there was any incompatibility among raw materials it should have been determined with the FTIR and DSC measurements. Oxide red colorant was tested with FTIR spectroscopy because we saw some compatibility problems with the solventborne bases. Measurements with FTIR and DSC methods showed no chemical reaction among the colorants and base paints (waterborne or solventborne) and also no chemical reaction among the raw materials in the colorants. We decided that FTIR and DSC measurements are not needed for orange and magenta colorants. The decision that FTIR and DSC measurements are not required with all of the four colorants was taken because we had already confirmed the required stability with rheological tests and the use in practice (dispensers). It is true that we saw a minor change in rheological behaviour with orange and magenta colorants, but this change did not affect the normal use in different systems (waterborne, solventborne) and in dispensers. Therefore we were more interested in finding out whether there is any chemical reaction with oxide red and solventborne products since there were some compatibility problems which need more attention to reach our final goal.

The final test, which took place after having determined that we had acceptable physically and chemically stable universal colorants, was checking the VOC content. We found some VOC content. At this point we started checking our raw materials and in fact saw that some of the VOC we got from dispersing agent 4 which was used in orange and magenta colorants. With the tests carried out for the purpose of this work it was not possible to find the precise content of VOC in raw materials we used in our formulation. Therefore the precise content of VOC will have to be determined for each raw material separately and in order to prepare universal VOC free colorants the colorant formulation should be made without that raw material.

We aimed at using similar raw materials with all colorants. Similar raw materials mean less problems at their final use (in the bases paint). We managed to prepare recipes with 4 different dispersing agents and with 9 different raw materials altogether - if we do not count pigments and filler-finntalc.

**Table 26:** Final recipes of filler paste and four universal VOC-free colorants.

Raw materials	Final versions				
	Filler paste V-8 [g]	Violet V-8A [g]	Magenta V-6 [g]	Red oxide V-6A [g]	Orange V-10 [g]
Water	34	3	40	8	26
Glycerol	2	3	6	5	8
Defoamer 1	1	1	1	0.5	1
Wetting and dispersing agent 1	2.5	6		5	
Dispersing agent 2	1.5			0.7	
Wetting and dispersing agent 3			12		15
Dispersing agent 4			0.5		0.2
FINNTALC	58				
Filler past version V-8		70		16	5
Pigment: Violet P.V.23		8			
Pigment: Magenta P.R.122			30		
Pigment: Red oxide P.R.101				61	
Pigment: Hybrid orange					40
Rubbing	20 minutes	40 minutes	40 minutes	40 minutes	40 minutes
Water		2	8	4	
Filler past version V-8			2		4.3
Deaerator 1	0.3	0.2	0.5		0.5



## 6. Conclusions

Our main aim was to prepare colorants that would meet the restrictions in the decorative paint industry. Searching for different answers through the work was not easy. We had to accept that to a certain degree some compromises will have to be made. That was especially evident in the solventborne system where we had some problems with the compatibility between the base and the colorants. That was with oxide red colorant. After we did the FTIR spectroscopy, DSC (different scanning calorimetry) and mix oxide red colorant in a base paint with other colorants (Figure 38), we agree that no further optimisation of that colorant was needed. Since all three methods including rheology show that oxide red colorant is stable.

Before testing the colorant in any base we had to prepare a stable colorant. We were testing the stability of the colorants in the stove at temperature of 40°C from 7 days to 4 weeks. We were checking a possible change with rheology measurements. After a colorant had passed the test with the stove and the stability had been confirmed with rheology tests, we made a step forward by checking the colorant in the paints. By checking the colorant in the paints we could perform many test and the results of these gave us the required information. With the paint we were checking the compatibility between the colorant and the paint base using rub-out test. The final test examined the stability of the colorant in the canister. Since we obtained the same information about the stability of the colorant with the rheology flow test as with the aging of the colorant in the dispenser, we can conclude that the information from the flow test is reliable and that testing in the dispenser is not necessary in the future for new colorants. This is important information since we do not need to wait for 3 months for the results from the dispenser.

The quality and choice of the colorants depends on the justified costs. Paint producers are always divided between the quality and the costs they can afford to have from the point view of their sale. For the purpose of this thesis we used cheap raw materials.

With the rheology and calibration tests conducted on the dispenser we could say we had four stable colorants. We were not sure if we had universal colorants until we performed compatibility and wetting testing. This had to be done in two different systems. One system was waterborne and the other solventborne. In each system we

were conducting wetting and compatibility tests on different products. Results showed that all the four colorants - violet, magenta, red oxide and orange - can be called universal waterborne colorants.

Further tests which showed chemical stability (DSC and FTIR) also indicated chemically stable colorants.

We did VOC (volatile organic compound) test as well. The content of VOC in our four universal colorants was between 4,4 to 9,5 grams per litre. Taking into account the fact that the current restriction is from 30 to 500 grams per litre for different decorative coatings, it is logical that our colorants are improving the VOC content in all base paints in which the VOC content is higher than 9,5 grams per litre. At the moment the limit of VOC for the solventborne enamels (interior) and therefore for solventborne colorants is 300 g per litre. For waterborne colorants we can conclude that VOC limit is 30 grams per litre if we want to mix interior wall paints. Our four universal colorants will be allowed to be used until the limit of VOC content goes below 9,5 grams per litre. Therefore the aim of our four universal colorants is currently reached and we can predict that it will stay so for at least the following few years. Normally we will base our research on these four universal colorants in order to prepare VOC free formulations for the future. Raw materials producers are also doing their best as to prepare the raw materials which would be VOC free and would at the same time provide the required quality. Our result with the VOC content also confirmed the fact that in research department no work in the paint industry is ever finished.

As mentioned, the market has different systems of colorants: waterborne, solventborne and universal. From our point of view we think that in the future it will be better to have universal colorants, which will have a very good quality in waterborne paints and an acceptable quality in solventborne paints. Achieving a good quality of waterborne paints means we are ready for the future in which solventborne paints will probably no longer be present in decorative colour industry. This means that dispensers will no longer need any cleaning. We have demonstrated in this master thesis that it is possible to prepare universal colorants which can be of good quality in both waterborne and solventborne systems. This was revealed with wetting, compatibility and analytical tests which indicate no chemical reaction between the colorants and the bases.

Producing coatings which have a minimum or no effect on the environment is what is expected from the paint producers. There are two main reasons dictating this. The first lies in the customers who are becoming more and more aware of the fact that people as the biggest population on the earth have the power either to destroy or to save the environment. This is why also the sales of waterborne products are rising. The second reason lies in the restrictions supported by scientific work. Hopefully our work will prove useful also to other paint producer since making products which have a minimum effect on the environment as well as its users should always be our goal.

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